



공학박사 학위논문

Flexible and Wearable Conductive Polymer Composite Strain Sensors for High-quality Body Motion Monitoring

고정밀의 신체 동작 모니터링을 위한 유연하고 착용 가능한 전도성 고분자 복합체 변형 센서

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서울대학교 융합과학기술대학원

응용바이오공학과

Liwei Lin

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지도 교수 박 원 철

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서울대학교 융합과학기술대학원 응용바이오공학과 응용바이오공학전공 Liwei Lin

Liwei Lin의 공학박사 학위논문을 인준함 2023년 6월

위육	붠 장	 <u>(인)</u>
부위	원장	 <u>(인)</u>
위	원	 <u>(인)</u>
위	원	 <u>(인)</u>
위	원	 <u>(인)</u>

Abstract

Flexible and Wearable Conductive Polymer Composite Strain Sensors for High-quality Body Motion Monitoring

Liwei Lin Department of Applied Bioengineering Graduate School of Convergence Science and Technology Seoul National University

Wearable and stretchable strain sensors have potential values in the fields of human motion and health monitoring, flexible electronics, and soft robotic skin. The wearable and stretchable strain sensors can be directly attached to human skin, providing visualized detection for human motions and personal healthcare. Conductive polymer composites (CPC) composed of conductive fillers and flexible polymers have the advantages of high stretchability, good flexibility, superior durability, which can be used to prepare flexible strain sensors with large working strain and outstanding sensitivity.

Firstly, a flexible, multi-functional, wearable, and conductive nanofiber

composite (WCNC) strain senor has been designed with handy preparation method. This work involves the elastic thermoplastic polyurethane (TPU) with decorated acid modified carbon nanotubes coupled silver nanowires (AgNWs) and solidified (ACNTs), polydimethylsiloxane (PDMS). The sequential decorations of ACNTs, AgNWs and PDMS enhance the conductivity, superhydrophobicity, and strain sensing performance of the TPU-based nanofibrous membrane. The WCNC (TPU/ACNTs/AgNWs/PDMS) possesses a quite low resistance about 1.22 Ω/cm^2 (conductivity is up to 3506.8 S/m), superior superhydrophobicity (contact angle is up to 153.04°) and self-cleaning property. Furthermore, the WCNC strain sensor possesses high sensitivity and large working strain (gauge factor is nearly 1.36×10⁵ with the working strain ranging from 38% to 100%), which illustrates that the WCNC has a quite large work strain under extremely high GF and has never been reported before. On account of its outstanding sensing performance, the WCNC can be used to monitor the different movements of human bodies and simultaneously monitor sensor signals in multiple vertical directions, achieving more accurate results.

Secondly, a multifunctional conductive nanofiber composite (M-CNC) strain sensor with reliable antibacterial property has been developed. The thermoplastic polyurethane (TPU) nanofiber is served as the substrate, decorated by acid modified carbon nanotubes (ACNT), and in-situ self-assembled silver nanoflowers (AgNF), entitling the M-CNC with double-shell conductive networks. The M-CNC (TPU/ACNT/AgNF) has a stable conductivity, which is up to 7.5×10^5 S/m. Further, the double-shell conductive networks have greatly enhanced the sensing performance of the M-CNC strain sensor, possessing a useful gauge factor of 55352, during the strain of 42% to 100%. Additionally, the outer

AgNF shell structure is stable even after the cyclic test for 1000 times under the strain of 50%. The AgNF also endow the M-CNC with great antibacterial property, indicating brilliant growth inhibition effects on Gram-negative Pseudomonas aeruginosa and Gram-positive Staphylococcus aureus.

Thirdly, a multifunctional conductive polymer composite (M-CPC) with great flexibility, high conductivity, and antibacterial property has been proposed. This research consists thermoplastic polyurethane (TPU) and synthetic silver nanoflowers (AgNF), which are embedded by hydroxypropyl methyl cellulose (HPMC). Actually, HPMC can achieve the excellent dispersibility of AgNF and establish a strong contacting between TPU substrate and HPMC/AgNF conductive film through hydrogen bonds. The M-CPC (TPU/HPMC/AgNF) exhibits high conductivity and cyclical stability. Further, the HPMC dispersed AgNF conductive network endows M-CPC with superior strain sensing performance, possessing an extremely high gauge factor (GF) of 2.8×10^7 (working strain: 30-35%), which is the highest GF of CPCs under small strains and has never been reported before. Additionally, HPMC/AgNF also makes M-CPC antibacterial, which has a relatively long-term antibacterial effect for 3 days.

Graphical abstract:



Keywords: Conductive polymer composites, Wearable strain sensors, Strain sensing performance, Body motion monitoring

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Chapter 1. Introduction of Conductive Polymer Composite Strain Sensors

1.1 Introduction

There is a growing demand for flexible electronic devices.¹⁻⁴ In particular, stretchable and wearable electronic devices are needed for multiple potential monitoring applications such as human health,⁵ body motion,⁶, ⁷ rehabilitation and soft robotics.⁸⁻¹⁰ Wearable strain sensors have attracted extensive attention because they can interact with the human body, reflect the health condition, and have long-term monitoring.^{11, 12} Wearable strain sensors can be attached to clothing or directly attached to human skin for human activity monitoring in real time.¹³⁻¹⁵ In addition to high efficiency, the strain sensors must meet some requirements of lightweight, high stretchability, good flexibility, reliable durability, low power consumption and biocompatibility.¹⁶ In the traditional preparation process, a large amount of solution is not deposited on the surface of the target substrates, but diffused into the surrounding air, especially when using volatile solvents, which not only causes waste, but also causes environmental pollution.^{17, 18} These requirements are stringent for mechanically compliant and highly stretchable strain sensors for human skin.^{18, 19}

It has been found that the conductivity of CPC varies with the change of inner conductive network of the polymer matrix.^{20, 21} When the CPC are stimulated by the external environment such as strain and temperature, the conductive network would be changed and the resistance would make a difference accordingly.²² Therefore, flexible CPC can be used as multifunctional response sensors to monitor external intervention, illustrating great application potentials in human motion monitoring,

fitness tracking and wearable interactive devices,^{23, 24} as shown in **Figure 1.1a.** According to the existing data on Web of Science, the research on CPC Strain Sensor has gone through 21 years (**Figure 1.1b**).²⁴⁻⁴¹ From the proposal of basic research methods at the beginning to the updating of flexible polymer materials and conductive fillers, the research enthusiasm is rising year by year. Especially around 2014, the CPC strain sensors became more and more sophisticated in design and performance.



Figure 1.1 (a) Wearable CPC strain sensors are promising in the field of human health detection, smart wound dressing and body motion monitoring.²⁴ (b) The developing timeline of CPC strain sensors. ²⁴⁻⁴¹ Figure used with permission from Lin, L. et al. ²⁴ Copyright © Elsevier, 2021.

1.2 Strain sensing mechanism

Conductive fillers are difficult to disperse and have little interfacial interaction, so it is difficult to form a uniform and stable conductive composite system. When the polymer is used at a relatively high temperature, it may soften or partially melt, which will not only destroy the network, but also destroy the stability and reliability of the sensing signals. Compared with traditional mechanical sensors, flexible and stretchable CPC strain sensors have greater flexibility, which can adapt to different working environments to a certain extent, and meet the deformation requirements of equipment and signal output.⁴² The stretchable strain sensor responds to the applied strain by different mechanisms depending on the substrates, micro-structures, conductive networks, and manufacturing process.43 Different from traditional mechanical sensors, mechanisms such as structural engineering, disconnection between conductive fillers, crack propagation and tunneling effects are used to develop flexible, wearable and stretchable CPC strain sensors.

1.2.1 Structural engineering

On Oct. 10, 2000, the Royal Swedish Academy of Sciences decided to award the 2000 Nobel Prize in Chemistry to Alan Haig and Alan MacDiarmid of the United States and Hideki Shirakawa of Japan for their discoveries of conductive polymers.^{44, 45} Since then, more and more researchers have been engaged in the development of conductive polymers and CPC. In the field of healthcare, wearable devices have attracted more and more attention due to their advantages of intelligence, high sensitivity and wide working strain.^{46, 47} Traditional metals and semiconductors were widely used as the strain sensor preparation materials, which has been unable to meet the growing medical and health demands, because of their poor biocompatibility, non-portability, inaccurate monitoring and other shortcomings. To tackle the obstacles, it is promising to develop wearable and stretchable CPC strain sensors that are flexible, low-cost, highly sensitive and easily to manufacture.

1.2.1.1 Blend doping

CPC are ideal choices for preparing wearable strain sensors due to their advantages of light weight, high conductivity, controllable conductive network and handy manufacturing.⁴⁸ One of the traditional methods for preparing CPC is conductive polymer modification, which is usually not used as the basic materials for strain sensors. The common approach is to mix conductive nanofillers directly into molten polymers, such as carbon nanotubes, graphene and metal nanoparticles, through blend doping.⁴⁹ Conductive nanofillers usually have very high surface energy, and are difficult to achieve great dispersion effect in molten polymer substrates, which tend to aggregate, negatively declining the mechanical property and conductivity of CPC. In addition, CPC generally exhibit low conductivity, as most nanofillers are wrapped by insulating polymers, which greatly impede electron transport. In addition to the direct doping of conductive nanofillers in the molten polymer substrates, CPC strain sensors can also be fabricated by permeating the elastomer polymer solution in the pre-constructed conductive network. CPC strain sensors prepared by blend doping usually have good strain sensing performance, but their applications in wearable strain sensors are severely limited due to the weak biocompatibility, poor air permeability and hard structure with large thickness.

1.2.1.2 Surface modification

To effectively avoid the increasing thresholds, decreasing conductivity, and improve the controllability and sensitivity of conductive networks, researchers have put forward the selective modification of conductive nanofillers on the surfaces of flexible polymer substrates, which contain the surfaces of polymer particles, fibers and membranes.^{20, 50} To some extent, the surface modifications of conductive nanofillers can avoid the hard issues of blend doping, which may cause agglomerations, blocking the inner conductive pathways. The commonly used surface modification method is to construct conductive network based on conductive ink by hot-pressing on the polymer substrate surface.⁵¹ In addition, modification of activated functional groups and subsequent grafting of conductive nanofillers on substrate surface has become a focus of research (**Figure 1.2a**). Here are some strain sensing performance comparisons of CPC with different manufacturing methods, as shown in **Table 1.1**.

Conductive nanofiber composites (CNC) are one kind of CPC. The initial preparation method of CNC is similar to blend doping, which is mainly obtained by electrospinning polymer solution containing conductive nanofillers.⁵² The conductive nanofillers are distributed in the polymer nanofibers through the electrospinning process, which have similar disadvantages with CPC prepared by blend doping, leading to the agglomeration of conductive nanofillers. As an alternative, conductive nanofillers can be selectively modified on the polymer nanofiber surface. In our previous study, we proposed to modify acidified carbon nanotubes by ultrasonication and silver nanoparticles by in-situ reduction on the surface of nanofibers.^{53, 54} Further, CNC have superior stretchability, porous structure, air permeability and skin affinity, which are potential candidates for the advanced wearable CPC strain sensors (**Figure 1.2b-d**).^{53, 54}



Figure 1.2 Four design strategies of CPC strain sensors: (a) TPU/HPMC/AgNF,41 (b) TPU/ACNTs/AgNPs/PDMS,⁵³ (c) TPU/ACNTs/AgNF,⁵⁴ TPU/ACNTs/AgNWs/PDMS.24 (d) (TPU: Thermoplastic Polyurethanes; ACNT: Acidified Carbon Nanotubes; AgNPs: Silver Nanoparticles; AgNF: Silver Nanoflowers; AgNWs: PDMS: Silver Nanowires: Polydimethylsiloxane; HPMC: Hydroxypropyl methyl cellulose) Figure used with permission from Lin, L. et al.⁴¹ Copyright © Elsevier, 2022. Lin, L. et al.⁵³ Copyright © Elsevier, 2020. Zhang, W. et al.⁵⁴ Copyright © Wiley-VCH, 2021. Lin, L. et al.²⁴ Copyright © Elsevier, 2021.

Polymer substrate	Conductive fillers	Working strain	Gauge factor	Ref.	
PVA	РА	100-140%	3.44	55	
Epoxy resin	CNTs	0.6-14%	6	56	
PMVS	CNTAs/CB	0-60%	10	57	
TPU	CB	0-20%	10.8	58	
PDMS	CB	0-10%	15.75	49	
PVA	SA/TA	180-200%	15.98	59	
Aramid/PVA	Polyaniline	100-130%	39	60	
TPU	Graphene pellets	50-100%	80	61	
TPU	SWCNT/RGO	200-300%	114.7	62	
PVA/gelatin	CB	0-18%	523	63	

 Table 1.1 Comparison of the strain sensing performance of CPC strain sensors extracted from literatures.

TPU	MWCNT	5-50%	5200	64
PA6/PVA	CB	0-40%	9706.9	65
OBC	CB	90-100%	1.40×10^{4}	66
TPU	CNT/AgNPs	200-250%	4.33×10 ⁴	67
TPU	CNTs/GNP	150-250%	1.30×10 ⁵	68
Fluoroelastomer	CNTs	85-100%	1.36×10 ⁵	69
TPU	HPMC/AgNF	30-35%	2.8×10 ⁷	41

(CB: carbon black; PA6: polyamide 6; PVA: poly (vinyl alcohol); CNTs: one-dimensional carbon nanotubes; MWCNT: multi-walled carbon nanotube; SA: sodium alginate; TA: tannic acid; OBC: olefin block copolymer; PA: phytic acid; PMVS: polymethylvinylsiloxane; SWCNT: single-walled carbon nanotube; RGO: reduced graphene oxide)

1.2.2 Slippage & disconnection

In the conductive thin layers fabricated by conductive nanofillers, electrons can pass freely through the well-developed overlapping conductive network.⁷⁰ The stretching of conductive network causes some of the nanofillers that are in contact with each other to lose their contact area, reducing the conductive pathways and thus increasing the resistance. From a microscopic point of view, the disconnection of the thin-layer conductive network organized by conductive nanofillers under stretching is caused by the slippage of nanofillers due to the weak interfacial bonding between nanofillers and stretchable polymer substrates.⁷¹ Recently, Jeong et al. put forward a stretchable CPC strain sensor with gold nanosheet (AuNS) and PDMS substrate, which has great durability due to hot-pressing fabrication.⁷² While being stretched, the AuNS based strain sensor can maintain their contact without experiencing any severe mechanical strain or von Mises stress, as show in Figure 1.3a. The slippage and disconnection mechanisms are usually used in the fabrication of ink-based CPC strain sensors, which are similar with stretchable electrodes and can form an effective contact with human body to detect dynamic signals.



Figure 1.3 Three typical stretching mechanisms: (a) Sequential microscope images and corresponding FEA results of percolated AuNSs under 0% and 50% mechanical strain.⁷² (b) Schematic illustration of the sensing mechanism of the CPC strain sensor with double conductive networks of ACNTs and AgNWs.²⁴ (c) AgNWs network at different strains for a high resistance strain sensor.⁴² (d) Schematic of the inner conductice network change in the Carbon Paper/PDMS composite during strain. Resistance changes of Carbon Paper/PDMS composite: (e) bending strain, (f) applied tensile strain and (g) compressive strain.⁷³ Figure used with permission from Jeong, S. et al.⁷² Copyright © Elsevier, 2020. Lin, L. et al.²⁴ Copyright © Elsevier, 2021. Amjadi, M. et al.⁴² Copyright © Wiley-VCH, 2016. Li, Y. et al.⁷³ Copyright © American Chemical Society, 2016.

1.2.3 Crack propagation

The brittle conductive networks outside the CPC are prone to stressinduced crack propagation, mainly in the stress concentrated area.⁷⁴ Currently, CPC strain sensors urgently need to achieve high sensitivity over a very large working strain. In general, cracks in the as-prepared materials are considered a sign of structural failure but constructing microcracked structures might be an effective way to achieve high sensitivity of CPC strain sensors. The researchers have been focusing on the design of the conductive networks and the protective coatings.⁵¹ In addition, our group came up with an innovative structure design. Onedimensional and two-dimensional conductive nanofillers are often modified on polymer substrate surfaces by spraying and hot pressing.⁷⁵ The conductive network constructed by our group is based on the selfassembly of AgNWs and densely packed to form a quasi-twodimensional conductive thin layer.²⁴ Because there still exists a large amount of AgNWs entangled together inside the gaps of nanofiber membrane, the external stress can realize the effective transfer to conductive network, which can maintain inner conductive pathways during large strains, achieving superior sensing performance (Figure **1.3b**). The advantage of using a dual conductive network is to maintain the overall conductivity of CPC under large strains. One-dimensional carbon nanomaterials are generally not sensitive to strain, and the conductive nanofillers that are prone to cracks and disconnections during strain should be constructed, which would lead to a large resistance change. As shown in **Figure 1.3c**, the single AgNWs conductive network would exist some bottleneck locations, which critically limited the conductivity during large strains, leading to the sharp but nonlinear increase of resistance signals.⁴² From a typical work made by Li et al.,
the network structure of carbon paper in the PDMS is critical to the performance of the strain sensor. Under a strain-free condition, carbon fiber network with few disconnections exists in the PDMS matrix. As the carbon fiber is tougher than PDMS, when the composite sensor encounters some deformations, disconnections and cracks start to appear in the carbon fiber network because it sustains much larger stress. Further, these disconnections gradually expand with an increase of the applied strain, which causes a decrease in the conductive paths and thus an increase in sensor resistance (**Figure 1.3d**). The relationships of $\Delta R/R_0$ with applied bending, tensile, and compressive strain are presented in **Figure 1.3e-g**, respectively. Under strain deformation, the $\Delta R/R_0$ of the sensor increases continuously, and two linear regions with different slopes are seen in a typical $\Delta R/R_0$ -strain curve.

1.2.4 Tunneling effect

Transit of electrons through the insulating barrier is called tunneling, which means electrons can tunnel through the polymer thin layer. The tunneling effect is often used to explain the sensing mechanism of CPC strain sensors fabricated by blend doping. With the increase of the tunneling distance and the destruction of the conductive pathways, the resistance of CPC increases significantly during the stretching process.⁷⁶ On the contrary, the conductive fillers can return to the initial position during the recovery process to reduce the tunneling distance and restore the conductive pathways. Thereby reducing the resistance of CPC, which exhibits detectable signals.

1.3 How to evaluate a wearable strain sensor

Strain sensing performance of CPC strain sensors are evaluated by different parameters, such as mechanical property, gauge factor, working strain, response time, durability, biocompatibility etc.⁷⁷ These

parameters are not the only determinant to performance of CPC strain sensors on the macro level, but more importantly, the unique design on the microstructure, which affects the strain sensing performance, additional functions and application potentials.

1.3.1 Mechanical property

Mechanical property is the basic performance of CPC strain sensors, which largely determines the durability and working strain of the sensors, affecting their application value.⁷⁸ The mechanical properties of CPC strain sensors are varied, among which the main ones are tensile and resilience. They depend on the types of polymer substrates, conductive fillers, inner structures, and manufacturing processes.^{79, 80} Generally, the mechanical properties of CPC prepared by blend doping are significantly poorer than that of polymer substrates. However, the mechanical properties of CPC prepared by surface modifications do not decrease obviously. Recently, Wang et al. reported the TPU/CB fibrous film strain sensor and detailed explained the stress-strain and sensing-strain curves.⁸¹ Usually, tensile testing is evaluated on a universal test machine with the speed of 5 mm/min (**Figure 1.4a and b**).



Figure 1.4 Strain sensing performance regarding GF, working strain, response time, and durability. (a) Schematics of the tensile test clamper with a sample and the tensile testing machine coupled with a Pico ammeter. (b) The normalized change in tensile stress and electrical resistance ($\Delta R/R_0$) vs. strain. (c) GF of the sample.⁸¹ (d) Resistance

response of the CPC strain sensor to gradually increasing strain from 0 to 450% and its GFs. (e) Response time of the CPC strain sensor to high-speed tensile deformations. (f) Durability of the CPC strain sensor for more than 1000 cycles. (g) The reversible sensing performance of the CPC strain sensor after 1000 cycles.⁸² Figure used with permission from Wang, X. et al.⁸¹ Copyright © Springer Nature, 2021. Zhou, H. et al.⁸² Copyright © Elsevier, 2021.

1.3.2 Gauge factor

Normally, researchers introduce the concept of gauge factor (GF) to express the sensitivity of strain sensors, and its calculation is GF= $(\Delta R/R_0)/\Delta\epsilon$, where ΔR represents the change of resistance and $\Delta\epsilon$ represents the working strain (**Figure 1.4c**).^{24, 83} It is noteworthy that the responsivity of the strain sensor is denoted by R/R_0 , where R and R_0 represent the transient resistance and the initial resistance.⁸⁴ For CPC strain sensors, it is normal to have more than two linear fitting curves due to the irregular change of conductive networks, which is mainly determined by the specificity of conductive fillers, so some strain sensors have different GFs under different strains (**Figure 1.4d**).

According to Table 1.1 and Table 1.2, the GFs of CPC prepared by surface modification are much higher than that prepared by blend doping. With further and in-depth research, researchers are unable to be satisfied with the GFs of CPC strain sensors that are less than 100. It means that the sensitivity of strain sensors is still far from practical expectations, hence they create new innovations on the conductive networks constructed by the inner conductive fillers. The key to improving GF depends on the precise design of the conductive network.⁸⁵ The common practice now is to use conductive nanofillers to construct nanoconductive networks. We can not only design different nano-conductive networks, but also realize the leap-forward improvements of GF by using conductive nanofillers with different dimensions and different morphologies. Additionally, conductive nanofillers with different dimensions can be used to customize different flexible polymer substrates. Our research group has designed the TPU nanofiber membrane-based CPC strain sensor with dual conductive networks containing one-dimensional ACNTs network and zero-dimensional

AgNPs network.⁵³ And the strain sensor possesses an extremely high GF of approximately 1.04×10^5 (with the strain from 20% to 70%), and they can be used to monitor both large and subtle joint movement. Table 1.2 lists the typical CPC strain sensors prepared by surface modification. We can clearly find that the CPC strain sensors using double conductive networks have a significant advantage in the sensing performance of high GF. Generally, the selection dual conductive networks of CPC strain sensors are complicated, mainly depends on the dimensional characteristics of conductive nanofillers. Commonly, 0-dimensional conductive nanoparticles, 1-dimensional conductive nanowires and 2dimensional conductive nanosheets are used. The combination of conductive networks with different dimensions usually results in high GF and large working strain. Actually, the conductive network composed of small-dimensional nanofillers is extremely sensitive to strain, resulting in the disconnection of the conductive network, but the sustainable strain range of the deformation is extremely small, which easily leads to the insulation of the overall composite under large strain. On the contrary, the conductive networks composed of largedimensional nanofillers can greatly make up for the shortcomings of the low-dimensional conductive network, especially their relative insensitivity to strain, which can maintain the overall conductivity of the CPC under large strain, so that the strain sensors would still have stable and detectable electrical signals (when the low-dimensional conductive network is destroyed by strain deformation).

Conductive fillers	Working strain	Gauge factor	Durability	Ref.
CNTs	50-100%	0.339	700 cycles (0-50%)	86
Graphene	95-100%	5.9	600 cycles (0-50%)	87
PANI	0-110%	17.15	unmentioned	88
SWCNT	50-100%	33	unmentioned	89
rGO	10-100%	79	6000 cycles (0-50%)	90
CNY	0-2%	1700	300 cycles (0-2%)	91
ACNTs and AgNPs	20-70%	1.04×10 ⁵	1000 cycles (0-70%)	53
AgNWs and ACNTs	38-100%	1.36×10 ⁵	1000 cycles (0-70%)	24
rGO and AgNWs	84-100%	4.4×10 ⁷	1000 cycles (0-10%)	92
	Conductive fillers CNTs Graphene PANI SWCNT i CNY ACNTs and AgNPs AgNWs and ACNTs rGO and AgNWs	Conductive fillersWorking strainCNTs50-100%Graphene95-100%PANI0-110%SWCNT50-100%rGO10-100%CNY0-2%ACNTs and AgNPs20-70%AgNWs and ACNTs38-100%rGO and AgNWs84-100%	Conductive fillers Working strain Gauge factor CNTs 50-100% 0.339 Graphene 95-100% 5.9 PANI 0-110% 17.15 SWCNT 50-100% 33 rGO 10-100% 79 CNY 0-2% 1700 ACNTs and AgNPs 20-70% 1.04×10 ⁵ AgNWs and ACNTs 38-100% 4.4×10 ⁷	Conductive fillers Working strain Gauge factor Durability CNTs 50-100% 0.339 700 cycles (0-50%) Graphene 95-100% 5.9 600 cycles (0-50%) PANI 0-110% 17.15 unmentioned SWCNT 50-100% 33 unmentioned rGO 10-100% 79 6000 cycles (0-50%) CNY 0-2% 1700 300 cycles (0-50%) ACNTs and AgNPs 20-70% 1.04×10 ⁵ 1000 cycles (0-70%) AgNWs and ACNTs 38-100% 4.4×10 ⁷ 1000 cycles (0-10%)

Table 1.2 Comparison of the strain sensing performance of TPU membrane based CPC strain sensors from literatures.

(PANI: polyaniline; CNY: carbon/graphene composites nanofiber yarn)

1.3.3 Working strain

Working strain is broadly interpreted as the strain range under which the strain sensor produces a stable GF.⁹³ Crucial here is linearity, as the nonlinear curve can make the calibration difficult. Therefore, the preparation of structurally ordered nano-conductive networks will be more capable of adapting CPCs strain sensors to complex strain conditions.⁹⁴ Accordingly, Li et al. prepared a wearable CPC strain sensor with two conductive networks through combined spray-coating of AgNW and GO.⁹² The GFs at the strains of 50-84% and 84-100% are 1.0×10^6 and 4.4×10^7 , respectively. The disadvantage of this CPC strain sensor is that it has an extremely high GF only under large strains. If CPC strain sensors can achieve extremely high GF under both small strains and large strains, they would have broad sensing application prospects.

1.3.4 Hysteresis effect

Hysteresis effect means that the fatigue crack propagation rate will be greatly delayed if the stress in one cycle is too high when the crack member is subjected to alternating load.⁸⁶ Minimal hysteresis becomes important when the CPC strain sensor is under dynamic load, especially when they are used for flexible and wearable devices.⁴² The large hysteresis may result in the irreversibility of the strain sensor under dynamic load. The hysteresis effect of CPC strain sensors is mainly caused by the viscoelastic properties of polymer and the interaction between the conductive nanofillers and polymer substrates.⁹⁰ The strong interfacial binding between soft conductive nanofillers and polymer and polymer substrate at high tensile. However, they cannot quickly slide back to their original position after fully releasing the strain, resulting in high hysteresis effect.

In contrast, the weak interface adhesions between rigid conductive nanofillers and polymer substrates are required for the nanofillers to fully return to its initial position upon release. This phenomenon must be paid attention to when designing the internal conductive networks of CPC strain sensor.

1.3.5 Response time

The response time reflects the time it takes for the signal output of the strain sensor to reach a steady state.⁹⁵ However, due to the viscoelasticity of CPC and the brittleness of the conductive network, most CPC strain sensors have different degrees of response delay.96 The CPC strain sensors with carbon nanomaterials as conductive fillers usually have a faster response time, while the response time of CPC strain sensors with metal nanomaterials as conductive fillers is relatively longer, which is around 150 ms. Table 1.3 illustrates the comparison of the response time of PDMS based CPC strain sensors with different conductive nanofillers. Additionally, CPC strain sensors processed by blend doping exhibit relatively longer response time because of the friction force between conductive fillers and polymer substrate, resulting in a slow speed of stretching and releasing of the inner conductive networks.⁹⁷ For instance. Zhou et al. have designed a CPC strain sensor composed of hollow polyaniline spheres (HPS), poly(vinyl alcohol) (PVA) and phytic acid (PA).⁸² Upon high-speed deformations, the CPC strain sensor exhibit a long response time of 0.22 s, as shown in Figure 1.4e.

Conductive polymer composite	Gauge factor	Response time	Ref.
		(ms)	
PDMS/Graphene/CNTs	35	30	98
PDMS/CNTs nanopaper	2.21	50	99
PDMS/silicone rubber/CNTs/CBs	1.25	60	100
PDMS/Carbon fragments	62.8	60	101
PDMS/CNTs/AuNPs	70	60	71
PDMS/CNTs	87	65	102
PDMS/PU sponge/NiNPs/rGO	3360	100	103
PDMS/PAVG	10.28	112	104
PDMS/PU fiber/AgNWs	9557	120	105
PDMS/CNFs/GNPs	7.04	132	106
PDMS/rGO	18.5	145	107
PDMS/TPU fibers/Aligned rGO	593	160	108

Table 1.3 Comparison of the response time of PDMS based CPC strainsensors extracted from literatures.

(CNF: carbon nanofiber; GNPs: graphene nanoplates; NiNPs: nickel nanoparticles; PAVG: parallelly aligned vertical graphene)

1.3.6 Durability

Durability represents the reliability and repeatability of the strain sensor to long-term stretching-releasing cyclic tests.¹⁰⁹ Whether it can have steady electrical signal output, mechanical transfer and morphological stability are the criteria for evaluating a qualified CPC strain sensor.¹¹⁰ Durability is even more important for wearable CPC strain sensors because they need to accommodate large, complex and dynamic strain deformations.¹¹¹ As shown in **Figure 1.4f and g**, most reported CPC strain sensors exhibit outstanding durability and stability during more than 1000 stretching and releasing cycles.

1.3.7 Biocompatibility

Wearable strain sensors are usually attached to clothing or in direct contact with human skin to obtain relevant human signals (Figure 1.5ae). The preparation process of CPC strain sensors is relatively simple, but the strain sensing abilities have good and regular curves, which can be suitable for monitoring a variety of body movements. CPC strain sensors should be biocompatible because of their wearable properties 113 clinical applications.^{112,} and the demand for potentially Biocompatibility is a broad biological concept, which can be more specific in the field of wearable devices.^{114, 115} Air permeability, comfort, skin affinity, no cytotoxicity, antibacterial property and no tissue adhesion are the biocompatibility required for wearable CPC strain sensors in the fields of human health monitoring and medical diagnosis.^{116, 117} If CPC strain sensors are developed that can accurately detect human health signals with superior biocompatibility, it would play a vital role in the innovation and promotion of modern medical diagnosis and treatment, greatly improving the development of intelligent health monitoring (Figure 1.5f).



Figure 1.5 Wearable and biocompatible CPC strain sensors for human health monitoring. The strain sensing performances and body motion

monitoring abilities of (a) Carbon nanotube (CNT) fiber/polyacrylamide (PAAm) hydrogel composite strain sensor,¹¹⁸ (b) Encapsulation of a carbonized nano-sponge (CNS) with silicone resin strain sensor,¹¹⁹ (c) Thermally expanded micro-spheres (TEM)/CNT/Ecoflex (TCE) sensor,¹²⁰ composite strain (d) Elastomer-wrapped carbon nanocomposite strain sensor, and (e) graphene nanoplatelet (GNP)/carbon nanotube (CNT)/silicone elastomer (GCE) fiber composite strain sensor.¹²¹ (f) The advanced and biocompatible CPC strain sensing system would ensure a convenient and timely way for portable healthcare.¹²² Figure used with permission from Yi, F. et al.¹¹⁸ Copyright © Elsevier, 2020. Yu, X. et al.¹¹⁹ Copyright © The Royal Society of Chemistry, 2017. Xue, S. et al.¹²⁰ Copyright © Elsevier, 2022. Tang, Z. et al.¹²¹ Copyright © American Chemical Society, 2018. Zhu, W. et al.¹²² Copyright © The Royal Society of Chemistry, 2022.

1.4 Perspective and outlook

Wearable and stretchable CPC can be assembled into strain sensors and applied in human health monitoring and medical diagnosis fields. A superior CPC strain sensor should have outstanding GF, especially under small strains. Further, long-term durability is necessary for CPC strain sensor during cyclic strains. Many high-performance CPC strain sensors can be developed by improving the properties and structures of flexible polymer substrates and conductive fillers, which have large working strain, high GF, minimal hysteresis effect and reliable durability. Deeper research in the future is likely to focus on several directions, as shown below.

1) Stable and sensitive conductive networks can be achieved by optimizing conductive nanofillers to accurately design conductive pathways, which would ensure the sensitivity and linearity of the CPC strain sensors.

2) Stretchable and flexible polymer substrates should be further developed with good biocompatibility, low price, uniform structure and superior mechanical property.

3) Wearable and adhesive CPC strain sensors should be designed through bionic structures, avoiding the use of artificial glue, to improve the wearing comfort and skin affinity.

4) The self-powered CPC strain sensor with wireless transmission should be designed for practical applications. Current signal processing circuits in flexible and stretchable sensing systems rely partly or entirely on rigid silicon chips, resulting in unnecessary stress generation and local strain imbalances.

1.5 Dissertation overview

This thesis has put forward the selective modification of conductive

nanofillers on the surfaces of flexible polymer substrates, which contain the surfaces of polymer fibers and membranes to effectively avoid the increasing thresholds, decreasing conductivity, and improve the controllability and sensitivity of conductive networks of CPC strain sensors.

In the first study, the acid modified carbon nanotubes (ACNTs) are firstly decorated on the electrospun thermoplastic polyurethane (TPU) nanofibers' surfaces to form the internal one-dimensional conductive network. Due to the effect of capillary action, the Ag nanowires (AgNWs) are spontaneously absorbed into the interspace of the TPU/ACNTs nanofibrous membrane and gradually self-assembled to form a compact and intertwining layer (thickness < 500 nm) on the nanofiber membrane surface. Therefore, the self-assembled AgNWs layer constructs a quasi-two-dimensional conductive network. Two conductive networks that are complementary in the spatial dimension are then initially established. Because of the fragility and vulnerability of the outer AgNWs layer, PDMS is introduced as a protective structure, which endows the obtained WCNC with superhydrophobicity and the properties of anti-harsh environments and self-cleaning. Note that as a glue, PDMS can not only stick AgNWs to form a stable layer, but also closely adhere the AgNWs and TPU nanofiber membrane together. The combined integration of the one-dimensional ACNTs network and the quasi-two-dimensional AgNWs layer network makes the WCNC possess a conspicuous conductivity (up to 3506.8 S/m). Even after multiple stretching-releasing processes (up to 1200 cycles with 70% strain), WCNC still shows the excellent stability owing to the strong interfacial adhesion. As a strain sensor, WCNC has extremely high sensitivity, GF is about 1.36×10^5 , and its working strain ranges from 38% to 100%.

WCNC strain sensor can monitor a variety of human joint movements even under harsh environments, and realize the simultaneous and more precise body motion monitoring in multiple vertical directions.

In the second study, this work continues to use acid modified carbon nanotubes (ACNT), which are easily to anchor through strong ultrasonication. Subsequently, a preliminary one-dimensional ACNT conductive network is formed on the TPU nanofibers surface, which has a large amount of active functional groups, such as -OH, -COOH. Based on this, a new method of in-situ modification and self-assembly to form silver nanoflowers (AgNF) has been proposed. With the increase modification times of in-situ self-assembly reductions, AgNF gradually grow on the surface of the nanofibers, and the AgNF petals are connected to each other to form a dense AgNF shell conductive network. M-CNC exhibits extremely high electrical conductivity (up to 7.5×10^5 S/m) due to the synergistic effect of two dual shell conductive networks of different dimensions (ACNT and AgNF). The electrical conductivity and surface conductive network structure of the M-CNC show superior stability even after multiple stretch-release cycles (up to 1000 times at 50% strain). Furthermore, the double-shell conductive networks endow M-CNC with outstanding sensing performance, possessing a large gauge factor of 55352 with the working strain ranging from 42% to 100%. M-CNC strain sensor can realize accurate human motion monitoring in multiple directions simultaneously on the same horizontal plane. In bacterial environments, AgNF endow the M-CNC with great antibacterial property, indicating brilliant growth inhibition effects on Gram-negative Pseudomonas aeruginosa (P. aureus, ATCC 27853) and Gram-positive Staphylococcus aureus (S. aureus, ATCC 25923). In the third study, the purpose of this part is to propose a new way that

can greatly improve the bonding effect of conductive nanofillers and flexible polymer substrates in the case of selective surface modifications, thereby greatly enhancing the performance of CPCs as strain sensors. In this paper, we innovatively put forward the traditional casting method to first prepare the AgNF embedded and dispersed by HPMC into a micronscale film conductive network, and then cast TPU on the upper part of HPMC/AgNF to obtain the TPU/HPMC/AgNF (M-CPC). Due to the formation of hydrogen bond interactions between TPU and HPMC, the AgNF dispersed by HPMC can be very firmly modified on the surface of TPU, thus owning excellent conductivity, strain sensing performance and cyclic stability. As a comparison, the physically selective surface modification to directly modify the AgNF conductive film on the TPU elastic substrate in the molten state has also been illustrated, and the related performance data has been further analyzed. However, TPU/AgNF exhibits very poor performances both in the stability of external AgNF networks and in the reliability of cyclic tests. Furthermore, the M-CPC possesses a high conductivity about 198 S/cm and extremely stable sensing signal output that can be monitored cyclically (more than 500 stretching-releasing cycles). Additionally, the HPMC dispersed AgNF conductive network endows the M-CPC with superior strain sensing performance, possessing a high GF of 2.8×10^7 during the working strain from 30% to 35%, which is the highest GF of CPCs under small strains and has never been reported before. It is worth noting that both TPU/AgNF and M-CPCs are endowed with outstanding antibacterial properties due to the existence of AgNF. However, due to the slow dissolution of HPMC in the bacterial growth environment, the HPMC dispersed and embedded AgNF can be released slowly along with the dissolution of HPMC, which has a relatively long-term antibacterial

effect, comparing with TPU/AgNF.

1.6 Reference

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Chapter 2. Superhydrophobic and Wearable TPU Based Nanofiber Strain Sensor with Outstanding Sensitivity for High-Quality Body Motion Monitoring

2.1 Motivation

In recent years, wearable strain sensors (WSS) have been widely applied in human health monitoring, soft robotics, biomedical engineering, human-computer interaction and other fields, especially the wearable devices with high sensitivity and high SNR (Signal-Noise Ratio).¹⁻³ In the field of medical care and health, wearable devices with the advantages of rapid preparation, adjustable sensitivity, and large detection range (working strain) have attracted more and more attention.4-6 Traditional metals and semiconductor materials are no longer sufficient to meet the increasing demand. To tackle this problem, conductive polymer composites (CPCs), which are flexible, low cost and easily processed, have become the promising candidates for strain sensors.⁷⁻⁹ Flexible CPCs are subject to certain external environments when applied as highly sensitive sensors, especially harsh environments such as acidic, alkaline, humidity, etc., which would result in molecular chain breakage, increased brittleness, decreased flexibility, and conductivity fluctuations. Recently, more and more researches have pointed to the introduction of superhydrophobic surfaces into CPCs, which can effectively improve their ability to resist harsh environments.^{10, 11} Further, conductive nanofiber composites (CNCs) have gradually become the more preferred substrates than CPCs due to their porous structures, excellent air permeability, skin affinity, large aspect ratio and so forth.¹²⁻¹⁵ The CNCs not only possess the superior

flexibility of CPCs, but also promote the innovations of preparing polymer matrix strain sensors.¹⁶⁻¹⁸ In our previous study, we proposed a way to induce conductive nanofillers to the nanofiber surface in the ultrasonic environment. One-dimensional conductive nanofillers were used as the conductive units, forming continuous conductive networks inside the CNCs.^{19, 20} To some extent, it avoids the hard issues of introducing the nanofillers directly into the polymer substrate through the some traditional methods like solution or melting process, resulting in the agglomerations and blocking the conductive pathways.²¹⁻²³

In common sense, conductive nanofillers exhibit different conductive properties in different dimensions due to their own structural characteristics. The crystals, conductive nanoparticles have extremely high conductivity in its original state, but in any other directions, they exhibit the characteristics like semiconductors or insulators, whose conductivity can differ by two or three orders of magnitude or more.^{24, 25} Therefore, in terms of their conductive properties, the substances can be regarded as a quasi-one-dimensional conductors.²⁶ Further, this kind of conductive networks will exist obvious conductivity change as the mechanical changing in any dimension.^{27, 28} However, the onedimensional conductive nanofillers, such as the silver nanowires (AgNWs) and carbon nanotubes (CNTs), have important applications in the fields of electronics, energy and optical devices because of its excellent electrical, mechanical and large aspect ratio properties.^{29, 30} As a flexible WSS, the most implicated performance measurement is the sensitivity (gauge factor and working strain). More and more research works have focused on exploring composite materials that produce high gauge factor (GF) and large working strain. We learned from the literatures that generally only one single conductive network cannot meet

the requirements of increasing both GF and working strain at the same time.^{12, 17, 31-38} Therefore, the simultaneous constructions of multiple conductive networks have gradually attracted the interests of researchers. Our previous work put forward a convenient preparation of CNCs with dual conductive networks (one-dimensional acid modified carbon nanotubes network and zero-dimensional Ag nanoparticles network). And the CNC-based strain sensor possesses reliable stability (> 1200 cycles under the strain of 70%) and a high GF value of 1.04×10^5 (strain range from 20% to 70%).¹⁷ Li et al. proposed a facile method to prepare a flexible strain sensor with two combined spray-coating conductive networks (one-dimensional AgNWs network and two-dimensional graphene oxide network). The GF of graphene oxide and AgNWs based strain sensor at the strains of 50–84% and 84–100% were up to 1.0×10^6 and $4.4 \times 10^{7.33}$ Nevertheless, most of the CNCs with multi-conductive networks still cannot achieve large working strain, high sensitivity, allround strain detection and ultrafast response at the same time, not to mention those CPCs with single conductive network. Therefore, it is very important to build multi-dimensional conductive networks to improve the sensing performance of CNCs. In the future, the research of CNC strain sensors will pay more attention to the innovations of conductive networks, especially for the sensing ability of subtle changes.

In this study, the acid modified carbon nanotubes (ACNTs) are firstly decorated on the electrospun thermoplastic polyurethane (TPU) nanofibers' surfaces to form the internal one-dimensional conductive network. Due to the effect of capillary action, the Ag nanowires (AgNWs) are spontaneously absorbed into the interspace of the TPU/ACNTs nanofibrous membrane and gradually self-assembled to form a compact and intertwining layer (thickness < 500 nm) on the nanofiber membrane

surface. Therefore, the self-assembled AgNWs layer constructs a quasitwo-dimensional conductive network. Two conductive networks that are complementary in the spatial dimension are then initially established. Because of the fragility and vulnerability of the outer AgNWs layer, PDMS is introduced as a protective structure, which endows the obtained WCNC with superhydrophobicity and the properties of anti-harsh environments and self-cleaning. Note that as a glue, PDMS can not only stick AgNWs to form a stable layer, but also closely adhere the AgNWs and TPU nanofiber membrane together. The combined integration of the one-dimensional ACNTs network and the quasi-two-dimensional AgNWs layer network makes the WCNC possess a conspicuous conductivity (up to 3506.8 S/m). Even after multiple stretching-releasing processes (up to 1200 cycles with 70% strain), WCNC still shows the excellent stability owing to the strong interfacial adhesion. As a strain sensor, WCNC has extremely high sensitivity, GF is about 1.36×10^5 , and its working strain ranges from 38% to 100%. WCNC strain sensor can monitor a variety of human joint movements even under harsh environments, and realize the simultaneous and more precise body motion monitoring in multiple vertical directions.

2.2 Experimental section

2.2.1 Materials and chemicals

Multi-walled carbon nanotubes (MWCNTs) were purchased from iCNT (diameter ≈ 20 nm, length: 1–25 µm), which were prepared through the CVD method. Nitric acid (HNO₃, 65-68%), sulfuric acid (H₂SO₄, 65-98%), tetrahydrofuran (THF, 99.5%), ethylene glycol (EG, 99.5%), polyvinylpyrrolidone (PVP, MW: 5500), heptane and toluene were obtained from Samchun Chemicals. N, N-dimethylformamide (DMF), Iron(III) choloride hexahydrate (FeCl₃·6H₂0), acetone and ethanol were

purchased from Sigma-Aldrich. Polydimethylsiloxane (SYLGARD® 184 SILICONE ELASTOMER KIT, PDMS) was purchased from Dow Corning. Thermoplastic polyurethanes (TPU) pellets were purchased from Shanghai Kai Sheng Plastic Co. Ltd.

2.2.2 Preparation of TPU nanofiber membrane

First, a certain amount of TPU pellets were weighed and dissolved in the mixed solution of DMF/THF (DMF:THF mixing mass ratio is 4:1). Then the mixed solution is heated to 60°C under magnetic stirring until a uniform TPU solution (concentration: 14wt%) is obtained, and then it is filled into a syringe that can be used for electrospinning. The mixed solution was then extracted at a rate of 1.0 mL/h from the metal nozzle connected to the high voltage supply (voltage: 15 kV). The distance between the metal needle nozzle and the drum collector was 12 cm. To collect the electrospun TPU nanofibers, we use the conductive aluminum foil, attaching it to the receiving plate. After spinning and forming the TPU nanofiber membrane, we removed the obtained membrane, and preserved it, cutting it into a suitable size for use.

2.2.3 Acid modification of CNTs and preparation of AgNWs

The acid modification of CNTs was performed as follows: firstly, 1 g CNTs, 60 mL sulfuric acid and 20 mL nitric acid were mixed in a 150 mL three-necked round bottom flask. Secondly, the mixture of CNTs was then stirred and evenly mixed, and the treatment maintained 15 min to form a well-dispersed solution. The mixture of CNTs was slowly heated slowly to 60 °C (time: 45 minutes) and stirred magnetically at this temperature with reflux for 3 h. Finally, we put the samples in an ice water bath and slowly add 800 mL deionized water. After standing for 12 h, pour the top liquid and wash the black samples on the bottom once

again. After repeating this operation three times, centrifugation and freeze-drying are performed to obtain acid modified carbon nanotubes (ACNTs).

AgNWs were synthesized by the reduction of the AgNO₃ in EG with PVP. Firstly, 10 ml EG was added to 0.205 g AgNO₃ and 0.467 g PVP, respectively, and then they were ultrasonic dispersed for 1 h to make fully dissolved. AgNO₃/EG was a transparent solution and PVP/EG was a viscous solution. After that, 50 μ L FeCl₃ solution with 0.1 mol/L concentration was added into the PVP solution and mixed with fully shaking. The PVP mixture was then slowly dropped into the AgNO₃ solution and transferred to a three-mouth flask. N₂ was then pumped into the three-mouth flask to ensure that the mixture was heated and reacted at 160 °C in an air-free oil bath. When AgNWs was generated (diameter \approx 50 nm, and length: 20-30 μ m), the color of the solution changed from yellow to gray. The suspension of AgNWs was centrifuged at 8000 rpm for 10 min. Finally, the AgNWs was washed with ethanol to remove the residual PVP and EG and refrigerated in ethanol at 5 °C.

2.2.4 Preparation of TPU/ACNTs and TPU/ACNTs/ AgNWs nanofiber composites

The ACNTs were pre-dispersed in a mixture of deionized water and ethanol (v/v: 1:1). We use an ultrasonic dispersing device (100-410-220, POWERSONIC) to stir and disperse for 10 minutes. For ACNTs, due to their large surface energy, they cannot be dispersed uniformly only by mechanical mixing. After that, ACNTs were anchored onto TPU nanofibers by the assistance of ultrasonication. During ultrasonication, ACNTs in the dispersion medium were intensively thrusted into the nanofibers and could be homogeneously embedded on the nanofiber surface. Finally, the TPU/ACNTs nanofiber membrane was dried in an

oven at 60 °C for 15 min. The final obtained WCNCs are denoted as TPU/X-ACNTs, where X represents the ultrasonic time (min) for preparing the TPU/ACNTs nanofiber composites.

In order to obtain the TPU/ACNTs/AgNWs nanofiber membrane, the prepared AgNWs were dispersed in ethanol and the concentration was controlled to be 25.0 mg·mL⁻¹. Due to the principle of capillary action, AgNWs are spontaneously absorbed into the gaps of nanofibers or assembly coated on the surface of TPU/40-ACNTs nanofiber membrane at room temperature, when the TPU/40-ACNTs nanofiber membrane was immersed in the AgNWs suspension. Furthermore, the color of WCNCs changed from black to gray. Therefore, a dense conductive network composed of AgNWs was constructed on the surface of the WCNCs. Finally, we used deionized water to remove impurities and dried them at room temperature. As Y represents the immersion time (min) of TPU/40-ACNTs in dispersed phase of AgNWs, TPU/40-ACNTs/Y-AgNWs is used to describe the obtained WCNCs after AgNWs modification.

2.2.5 Preparation of the superhydrophobic TPU/ACNTs/ AgNWs/PDMS nanofiber composites

At room temperature, the PDMS and curing agent were mixed in nhexane at a mass ratio of 10:1, and magnetically stirred for 25 minutes under dark conditions to finally form a 1wt% PDMS solution. Then the TPU/40-ACNTs/30-AgNWs were soaked in PDMS solution for different time, dried and cured in a vacuum oven at 80°C for 2 hours. The prepared WCNC is TPU/40-ACNTs/30-AgNWs/Z-PDMS, which has superhydrophobicity, self-cleaning and anti-crossive properties. Z is the PDMS modification time (min) of TPU/40-ACNTs/30-AgNWs. Note that TPU/40-ACNTs/30-AgNWs/45-PDMS is the final WCNC sample obtained after experimental explorations, used for the characterizations and performance tests.

2.2.6 Characterization

The surface morphologies, composite structures of samples were examined by the microscope (Nikon ECLIPSE, LV100) and the field emission scanning electron microscopy (FESEM, Hitachi S-4800), with energy-dispersive X-ray (EDX) spectrometry, X-ray diffraction (XRD, Bruker D8 Advance with Cu k α radiation λ =0.15406 nm) and Fourier transform infrared (FT-IR) spectroscopy (ALPHA, BRUKER, Karlsruhe, Germany). Amount of different compositions in TPU/ANCTs/ AgNWs/PDMS were determined by Thermal gravimetric analysis (TGA, Mettler Toledo).

2.2.7 Conductivity and contact angle measurements

We used the four-probe resistance tester (CMT-100S) to measure the surface resistance and conductivity of different WCNCs. For each sample, we select 5 different locations on the surface and average the measured values to determine the conductivity and its error range.

The static solution contact angles of WCNCs were measured with an electro-optical contact angle measuring instrument (Phoenix-150). The standard water droplet of 5 μ L was used to analyze the hydrophobicity of WCNCs. Averaging the 5 measurements at 5 different positions on the surface of WCNCs to obtain CAs.

2.2.8 Electrical signal measurement of strain sensing

Strain sensing sensitivity is the most important evaluation criterion for strain sensors. The WCNC samples were installed with copper wires by silver paste and connected to a resistance meter (Tes-2700), which can instantly monitor the resistance change of WCNCs in the process of stretching and releasing. It is worth noting that the transient resistance (*R*) and initial resistance (R_0) of the WCNC sample will occur during the stretching-releasing process, so the response value of the strain sensor is represented by R/R_0 . Normally, researchers introduce the concept of gauge factor (GF) to express the sensitivity of strain sensors, and its calculation is GF= $(\Delta R/R_0)/\Delta \varepsilon$, where ΔR represents the change of resistance and $\Delta \varepsilon$ represents the strain of the sensor.

Please note that in order to obtain a stable initial resistance, we prestretched the WCNC sample for 20 times before recording the sensing signals. In actual strain sensing applications, conductive fillers with lower initial resistance but larger resistance change (ΔR) are used to construct a sensitive conductive network, which is beneficial to improve strain sensitivity.

2.2.9 In vitro cytotoxicity test

In order to determine cytotoxicity and cell proliferation rate, L929 cells and HSF cells were cultured in each cell culture system for 24 hours, and samples were taken for water-soluble tetrazolium (WST) assay and Live/Dead cell staining assay.

2.3 Results and discussion

The wearable conductive nanofiber composites (WCNCs) are consisted of a TPU/ACNTs substrate layer, a dense AgNWs layer and a transparent PDMS layer as shown in **Figure 2.1a**. The synergistic effect of multilayered structure endows WCNCs with great superhydrophobicity and conductivity. The morphology of ACNTs was analyzed by the field emission scanning electron microscopy (**Figure 2.2a**). Using the driving force of ultrasonic waves to forcibly assemble rigid and high surface energy ACNTs onto TPU nanofibers. From a macro view, this process was based on the collision and interaction between ACNTs and TPU nanofibers, which are smooth and viscoelastic, resulting in the binding
force.³⁹ From a microscopic view, the acidified groups in ACNTs may combine with the TPU macromolecules through hydrogen bonds, which is more conducive to the decoration of coating ACNTs onto TPU nanofiber surfaces. ACNTs are attached or buried on the TPU nanofiber surfaces, which become rougher after the ACNTs modification (Figure 2.2b). Since then, the first one-dimensional conductive network of ACNTs has been constructed on TPU nanofibers and produced a preliminarily conductive effect. After constructing the one-dimensional ACNTs network, we considered the AgNWs with extremely high conductivity and excellent stability to build another independent hierarchical conductive network. As shown in Figure 2.3a, the prepared AgNWs suspension is gray, and microscope image has obvious metallic luster. With the increase of the reaction time for preparing AgNWs, we found that the lengths are 10 µm (time: 15 min) and 30 µm (time: 30-45 min), respectively, as shown in Figure 2.3b-d. Therefore, we chose the longer AgNWs (time: 30 min), which can self-assemble to the gaps and the outer surface of the nanofiber membrane by immersion, forming a quasi-two-dimensional AgNWs layer network.⁴⁰ Due to the existence of the dense AgNWs layer packed on the WCNC surface, both conductivity and hydrophobicity of WCNC have been further improved. Such two independent but synergistic multi-dimensional conductive networks endow the TPU nanofiber membrane with high conductivity, making the whole nanofiber composites present a large aspect ratio, and the conductive networks are constructed in both the inner and outer parts. The self-assembled AgNWs layer network is fragile and easy to peel off, hence we introduced the low surface energy PDMS as a protective structure to overcome the weak interfacial interaction between the individual AgNWs. The final obtained WCNC emerges a gray surface

and the water droplet can stand on it (CA $\geq 150^{\circ}$), as shown in Figure **2.1b** and the inset. The WCNC maintains the initial flexibility and bendability of TPU nanofiber membrane (Figure 2.1c). The thickness of WCNC is about 0.188 mm (Figure 2.1d), and the original resistance is about 3.1 Ω (Figure 2.1e). Thanks to the PDMS glue, as a fragile network with weak interfacial interaction, the PDMS modified AgNWs can stick with each other closely, and firmly attach to the WCNC surface (Figure 2.1f). The element distribution of the WCNC is revealed by energy-dispersive X-ray (EDX) spectrometry. It can be seen that C, O and N are distributed in whole composites due to the uniformity of electrospinning and ultrasonic modification, while Si and Ag are mostly distributed on the outer part of WCNC (Figure 2.1g-k).



Figure 2.1 (a) Schematic diagrams of the fabrication process of the multi-layered and superhydrophobic TPU/ACNTs/AgNWs/PDMS strain sensors. (b) Photograph of prepared WCNC (The inset is the solid-liquid-gas contacting state of the WCNC membrane surface). (c) Photograph of the WCNC with good flexibility. (d) Photo showing the thickness of WCNC membrane. (e) Photo illustrating the resistance of WCNC membrane. (f) SEM image for the cross-sectional structure morphology of the WCNC. (g-k) Elemental mapping images of carbon, nitrogen, oxygen, silver, and silicon.



Figure 2.2 SEM images of (a) the pure ACNTs, (b) the TPU/ACNTs nanofibers after 40 min ultrasonication.



Figure 2.3 (a) Photograph of the AgNWs suspension. SEM images of the AgNWs under different recation times: (b) 15 min, (c) 30 min and (d) 45 min.



Figure 2.4 Contact angle and conductivity of the WCNCs as a function of (a)TPU/X-ACNTs, (b) TPU/40-ACNTs/Y-AgNWs and (c) TPU/40-ACNTs/30-AgNWs/Z-PDMS. (d) Electrical conductivity of TPU/40-ACNTs, TPU/40-ACNTs/30-AgNWs, TPU/40-ACNTs/30-AgNWs/45-PDMS and TPU/30-AgNWs/45-PDMS, respectively.

The conductivity of TPU/ACNTs is positively correlated with the ultrasonication time X. When X comes to 40 min, the conductivity reaches 0.099 S/m, and then tends to remain unchanged (**Figure 2.4a**). Interestingly, the CAs of TPU/ACNTs are stable during the ultrasonication, which are around 100°. When TPU nanofiber is densely attached with ACNTs, its surface roughness is further improved, leading to the improvement of hydrophobicity. Although ACNTs have some hydrophilic functional groups, the composite material still possesses hydrophobic.

The surface of the TPU nanofiber membrane is smooth and flat, while the interior is porous nanostructure. As shown in **Figure 2.5a-c**, the capril-guided AgNWs can be spontaneously adsorbed into the pores and gaps of the TPU/ACNTs nanofiber membrane. With the increase of modification time, the saturated AgNWs suspension environment provides enough AgNWs, which are gradually self-assembled onto the surface of TPU/ACNT nanofiber membrane, forming a nano-scale layer of AgNWs, as mentioned in **Figure 2.1f**. In detail, the conductivity and CA of TPU/40-ACNTs/10-AgNWs are around 2222.9 S/m and 117.8° (**Figure 2.4b**). When more and more AgNWs are self-assembled onto the WCNC surface, the color changes from black to gray, while the conductivity and contact angle gradually increased to 3587.9 S/m and 121.8°, respectively, and then remained almost unchanged. It can be proved that when the modification time Y of AgNWs comes to 30 min, the outer AgNWs layer becomes a saturated state.



Figure 2.5 SEM images of the WCNCs morphologies of TPU/40-ACNTs/Y-AgNWs (different modification time of AgNWs) and TPU/40-ACNTs/30-AgNWs/Z-PDMS (different modification time of PDMS). Y: (a) 5 min, (b) 30 min and (c) 60 min; Z: (d) 5 min, (e) 45 min and (f) 90 min. (g) XRD patterns, (h) FT-IR spectra and (i) TGA of different WCNCs.

Furthermore, PDMS is a low surface energy colloidal substance, which is coated on the outer AgNWs layer of WCNC (Figure 2.5d-f). Since the quasi-two-dimensional layer is composed of single AgNWs, its outer surface has extremely high roughness. Combining the properties of the two substances endows WCNC with superhydrophobicity. In addition, the dense AgNWs layer can effectively prevent a large amount of PDMS from invading the TPU/ACNTs nanofibers inside the WCNC in a short time ($Z \le 45$ min). As mentioned in Figure 2.1k, the element mapping image for Si can support this view. Figure 2.6 illustrates the morphology of the TPU/40-ACNTs/30-AgNWs nanofibers before and after PDMS modifications. We stretched the WCNCs at the strain of 30% and detected the morphology of the TPU/ACNTs nanofibers inside the cracks. We found that there is no obvious PDMS coating on the nanofibers in Figure 2.6e and f, despite the PDMS has already modified. On account of the low conductivity of TPU/ACNTs, it would cause the internal onedimensional conductive network losing its conductivity, if a large amount of PDMS is modified on the surface of the internal nanofibers. As shown in Figure 2.4c, during the first 45 min, the conductivity of WCNCs is almost maintained around 3500 S/m. However, in the next 45 minutes, there exists a slump in conductivity, from 3506.8 to 627.1 S/m. On the contrary, the CA exhibits a significant upward trend with the increase of Z, from 139.81° for TPU/40-ACNTs/30-AgNWs/5-PDMS to 153.04° for TPU/40-ACNTs/30-AgNWs/45-PDMS, then remains almost unchanged afterwards. The conductivity of TPU/ACNTs is extremely low, while after the quasi-two-dimensional AgNWs layer is constructed, the conductivity of WCNC has increased by nearly 6 orders of magnitude (Figure 2.4d). Although the insulating PDMS is modified, the conductivity declines between TPU/40-ACNTs/30-AgNWs/45-PDMS

and TPU/40-ACNTs/30-AgNWs is quite slight, from 3587.9 to 3506.8 S/m. In contrast, the CNC constructed with single AgNWs layer has a much lower conductivity than the WCNC under the simultaneous effect of the multi-dimensional conductive networks, and the conductivity of TPU/30-AgNWs/45-PDMS is only 56.6 S/m.



Figure 2.6 SEM images taken at different scales of TPU/ACNTs/ AgNWs: (a) 50 μ m (b) 20 μ m (c) 1 μ m and TPU/ACNTs/AgNWs/PDMS: (d) 50 μ m (e) 20 μ m (f) 1 μ m under the strain of 30%.



Figure 2.7 Typical stress-strain curves of TPU nanofiber membrane and its composites.

The crystal structure of TPU and its composites was investigated by Xray diffraction (XRD), as shown in Figure 2.5g. First of all, a wide diffraction peak is generated when the 2theta degree is around 20°, which belongs to TPU. After the ACNTs further modified, the wide diffraction peak becomes more pronounced and occurs between 16° to 23°. In contrast, when the AgNWs layer is modified on the TPU/ACNTs nanofiber membrane, the intensity of the diffraction peak belonging to TPU is weakened, but obvious and sharp diffraction peaks are exhibited at 38.3°, 44.5°, 64.7° and 77.5°, corresponding to the 111, 200, 220 and 311 crystal planes of AgNWs.⁴¹ FT-IR spectra is used to characterize the functional groups and intermolecular interactions between the phase components of TPU nanofibers and their composites, as shown in Figure **2.5h**. For the TPU nanofiber membrane, due to the characteristics of its polymer composition and structure (N-H and C-O-C groups of urethanes), characteristic peaks are generated at 3333 cm⁻¹ and 1072 cm⁻¹ ¹. Additionally, the characteristic peak at 2952 cm⁻¹ is the stretching vibration of -CH₃. The two absorption peaks at 1728 cm⁻¹ and 1529 cm⁻¹ ¹ correspond to the -H-N-COO- group. After the one-dimensional ACNTs network was modified on the surface of TPU nanofibers by ultrasonic adsorption, the characteristic peaks at 1728 cm⁻¹ and 1529 cm⁻¹ ¹ shifted slightly. The interfacial interactions between TPU nanofibers and ACNTs are similar to hydrogen bonds.⁴² For the final obtained TPU/ACNTs/AgNWs/PDMS nanofiber composite, by virtue of the construction of PDMS protective layer, WCNC exhibits some characteristic peaks based on silicon. The two characteristic peaks at 1085 cm⁻¹ and 1023 cm⁻¹ are attributed to the stretching vibration of Si-O. The weak peaks at 792 cm⁻¹ and its vicinity are mainly due to the existence of Si-C structure, which are the stretching vibration of Si-C

and the swing vibration of Si-(CH₃)₂.^{36, 43} As shown in Figure 2.5i, the thermal stability and components of WCNC are evaluated by thermogravimetric analysis (TGA). TPU/40-ACNTs, TPU/40-ACNTs/ 30-AgNWs and TPU/40-ACNTs/30-AgNWs/45-PDMS are thermally degraded under air condition, their residual weight percentages at 800 °C are 2.97%, 7.54% and 11.69%, respectively. Because each component is modified step by step, the differences illustrate that the weight percentage of AgNWs in TPU/40-ACNTs/30-AgNWs is about 4.57%, and the PDMS in TPU/40-ACNTs/30-AgNWs/45-PDMS is about 4.15%. Obviously, the TGA curves of the WCNC modified with the dense AgNWs layer and the PDMS protective layer move to the high temperature region.⁸ AgNWs layer and PDMS layer have improved not only the hydrophobicity and conductivity but also the mechanical properties of WCNCs. As seen in Figure 2.7, Obviously, the elongation at break of the WCNCs exhibit a remarkable improvement from 462.42% to 508.50%, after the introduction of AgNWs. Note that the enhanced interfacial adhesion by PDMS is beneficial to the stress transfer during stretching, leading to the high tensile strength about 10.98 MPa and thus the improvement of the mechanical properties.



Figure 2.8 (a_1 - a_6) Photographs of dynamic tests of water-adhesion between the syringe needle and the WCNC surface (5 μ L water droplet). (b-d) Self-cleaning process on the surface of WCNC.



Figure 2.9 Photographs of the WCNC membrane under different tensile strain ($\epsilon = 10\%$, 30%, 50% and 70%) with spherical water droplets standing on the surfaces.

As mentioned above, the low surface energy PDMS layer makes WCNC superhydrophobic. As shown in Figure 2.8a₁, a water droplet attached to the nozzle of the metal needle by surface tension gradually approaches WCNC and eventually touches the surface (Figure 2.8a₂ and a₃). Unexpectedly, the water droplet remains the standing state and are not absorbed by the surface of WCNC even if it is squeezed in both directions (Figure 2.8a₄). Furthermore, when we lift the needle, the water droplet moves quickly away from the surface of WCNC (Figure 2.8a₅ and a₆), displaying superior water repellence. Additionally, TPU/40-ACNTs/30-AgNWs/45-PDMS also has a very low sliding angle except for high CAs. This means that the water droplets can roll freely on the tilted WCNC surface, thereby absorbing the surface stains. If so, we can conclude that WCNC has the excellent self-cleaning property. CNTs powders used as model pollutants are deposited on the surface of WCNC (Figure 2.8b). After that, a small amount of water is then dripped slowly onto the WCNC surface (Figure 2.8c). With the help of a dropper, they can easily roll over the surface. During this process, CNTs powders are gradually adsorbed by the rolling water droplets (Figure 2.8d). Finally, all CNTs powders are carried by the rolling droplets away from the WCNC surface (Figure 2.8e).

It is well known that mechanical deformation often occurs in the actual use of strain sensors, and such this process would bring irreversible damage to them. **Figure 2.9a** illustrates the contact states of water droplets on the WCNCs surfaces, when doing some stretches under different strain of 0%, 30%, 50% and 70%. Although the different stretch could damage the outer conductive AgNWs layer, the cracks and dots generated on the WCNCs surfaces (**Figure 2.9b-d**), could further improve the surface roughness, bringing about the growing tendency of

the CAs. Obviously, even under the strain of 70%, the water droplets still remain spherical on the WCNC surface, exhibiting excellent superhydrophobicity. Despite of some subtle fluctuations, the CAs slightly increase with the strain, reaching up to 154° at $\varepsilon = 70\%$ and then dropping to 153° at $\varepsilon = 100\%$ (Figure 2.10a). For further verification of the corrosion resistance and stability of WCNC, we set it in an acid solution (pH=1). Without the external pressure, WCNC can float on the acid solution, either by the surface or side, which further demonstrates its superhydrophobicity, as shown in the inset of Figure 2.10b. It can be seen from Figure 2.10b that the CAs remain almost unchanged during the first 2 hours of soaking, and slightly decreased to 150° in the next 6 hours. As the immersion time further increases, CAs fluctuate around 150°. For another thing, the conductivity is stable throughout the anticorrosive test, almost maintaining the initial value, due to the protection of the conductive network by PDMS. It can be seen that the strong acid solution will slowly oxidize the PDMS layer, resulting in some chain scissions between Si-O-Si bonds.44 In addition, we also performed a dynamic test for the adhesion of acid solution droplets between the injection needle and the WCNC surface (Figure 2.11), illustrating the outstanding anti-corrosive resistance and superior superhydrophobicity. It can be seen from Figure 2.10c that the corrosive acid, base, and salt droplets can stably maintain their spherical shapes on the surface of the WCNC. Under various adverse conditions, the CAs of WCNC are around 153°C (Figure 2.10c), indicating that our WCNC has anticorrosive resistance.



Figure 2.10 (a) CAs of the WCNCs under different stretching strain. (b) The change of CAs and conductivity of WCNC during the time to endure the acid solution. (c) Four different kinds of solutions dropped on the surface of the WCNC and the measurement of CAs. The conductivity and CAs of WCNCs after different times of mechanical deformation in different dimensions: (d) deposing to cyclic stretching-releasing under the strain of 50%, (e) hammer striking in longitudinal direction, (f) bending the WCNC for more than 135°.



Figure 2.11 Photographs of contacting, pressing, and departure processes of a 5 μ L acid droplet (pH = 1) on the WCNC surface.

We find that the mechanical strain in the plane dimension (twodimensional) has minor influence on the conductivity and CA of the WCNC. Figure 2.10d illustrates the changes in CAs and conductivity of WCNC after different times of cyclical tensile tests under 50% strain. Although there exist some small fluctuations in the CAs, they remain at 153° throughout the cyclical test. The conductivity tends to be an unconspicuous decrease during the first 20 cycles. Further, it remained nearly unchanged at the next 60 cycles. Furthermore, the most surprising is that we have selected 5 different locations of WCNC for testing each time, and the results are quite similar and the errors are extremely small. In contrast, when we apply mechanical deformations other than twodimensional to WCNC, such as hammer striking (Figure 2.10e) and large bending (Figure 2.10f), we find that the CAs of WCNCs are still stable at 153°, and the average conductivity is maintained at the original state about 3500 S/m. It is worth noting that the conductivity measured at different positions has a certain range of differences, but the WCNCs still have the high performance of conductivity. After all, the PDMS protective layer provides strong interfacial interactions for the quasitwo-dimensional AgNWs layer network, which is a planar hierarchical structure that are vulnerable and sensitive to mechanical deformations in the vertical dimension. Figure 2.12 illustrates the typical curves of timedependent weight loss of the water at 50 °C (heating by an infrared lamp). Evaporation rates can be calculated from the wright loss curve. For the WCNC, the water evaporation rate is $0.56 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, demonstrating the breathability.45



Figure 2.12 Weight loss of the water caused by the escape of the evaporation generated vapor through the WCNC over time at 50 °C.



Figure 2.13 Strain sensing performance of the WCNCs under (a) $\varepsilon = 10\%$, (b) $\varepsilon = 30\%$, and (c) $\varepsilon = 50\%$ at a strain rate of 50 mm·min⁻¹.

The strain sensing performance of WCNCs is demonstrated by the resistance response, which is represented by the ratio of instant resistance (R) to initial resistance (R_0), denoted as R/R_0 . Figure 2.13 illustrates the periodic signals of WCNC when launching some small deformation stretching, such as 10%, 30% and 50%. We can find that the change of sensing intensity (R_I : maximum R/R_0) is positively correlated with the increase of stretching ratio, which are 2.2, 4.5 and 22.1 at the strain of 10%, 30% and 50%, respectively. Further, larger strains are applied to WCNC. As expected, under the strain of 70%, the R_I takes a leap, reaching 17911.1. Since the quasi-two-dimensional AgNWs layer network modified by PDMS exhibits excellent stability, accompanying with the internal one-dimensional ACNTs network, the WCNCs are endowed with the great strain sensing stability, and the output signals also show excellent reproducibility (Figure 2.14a). As shown in Figure **2.14b**, we have selected three parts from the front section, middle section and rear section among the 1200 cycles, and further analyzed the strain response signals. It is found that the $R_{\rm I}$ remains almost unchanged in the two intervals from 250 s to 495 s and 2400 s to 2645 s, while there exists a slight increase in the interval from 4500 s to 4745 s. When the strain increases to 100%, the corresponding $R_{\rm I}$ has a further improvement, reaching 87331.0, as shown in Figure 2.14c. The main factor causing the sharp rise of the resistance is that the quasi-two-dimensional AgNWs layer network has been further destroyed by large strain, but the internal one-dimensional ACNTs network still maintains a tangled state. So the WCNC remains to be conductive even under large strain. Figure 2.14d shows that within same duration, the changes of R/R_0 and displacement of the deformation present synchronization and consistency, emerging the low signal-to-noise ratio and instant sensing performance of WCNC

as a strain sensor. According to **Figure 2.15**, the response time and recovery time of WCNC were 181 ms and 153 ms at a high tensile speed of 1500 mm/min under the strain of 30%. This rapid response and recovery time ensure that fast and continuous movements can be monitored in real time.



Figure 2.14 (a) Durability test of WCNC under repeated 70% strain for more than 1200 stretching and releasing cycles. (b) Cyclical resistance changes at the front, middle, and end of the durability test under $\varepsilon = 70\%$. (c) Strain sensing performance of the WCNCs under $\varepsilon = 100\%$ at a strain rate of 50 mm·min⁻¹. (d) The change of *R*/*R*₀ and the displacement of the deformation during stretching-releasing process. (e) Two linear fitting curve (0% < ε < 38% and 38% < ε < 100%). (f) Comparison of strain sensing performance including maximum gauge factors and working strain of various nanofiber composites.^{12, 17, 31-37}



Figure 2.15 Response time and recovery time of the WCNC under a strain of 30% with the stretching rate of 1500 mm \cdot min⁻¹.

As shown in Figure 2.14e, in the initial strain range ($0 < \varepsilon < 38\%$), the resistance change shows a linear increase but the growth rate is quite slow. This is mainly because the quasi-two-dimensional AgNWs layer network coated on the outer part of WCNC. The dense AgNWs are entangled with each other to maintain the conductive network under the small strain. Although it is subjected to stress transmission, small strain cannot cause major damages to the dense hierarchical structure, so the GF is calculated to be 7930. During the larger strain range (38% < ϵ < 100%), the quasi-two-dimensional AgNWs layer network has been seriously damaged, but the one-dimensional ACNTs network still remains entangled and maintains the original conductive path. The resistance change of WCNC shows a rapid linear rise, the GF is calculated to be 136516. Our WCNC has a similar GF change law as many nanofiber-based strain sensors. According to the current literature, WSS based on flexible conductive nanofiber composites have a highest GF up to 4.4×10^7 , but its working strain is only from 84% to 100%.³³ Additionally, the nanofiber-based WSS with the largest working strain can even reach 0-900%, but GF is only 19.96.46 Our previous work has constructed a dual conductive network structure of CNCs, with a high GF of 1.04×10^5 and a working strain of 20%-70%.¹⁷ This is the only work reported in the literature that can meet the requirements of both high GF and large work strain (Figure 2.14f). Therefore, our proposed WCNC has great application potential, due to its high GF of 1.36×10^5 and large working strain from 38% to 100%. The further comparisons of the nanofiber-based WSS are summarized in Table 2.1.

Matrix	Conductive fillers	Working strain	Gauge factor	Cyclic stability	Author & Ref.
TPU	CNTs	50-100%	0.339	700 cycles (0-50%)	Wang et al. ¹²
TPU	Graphene and SiO ₂ NPs	95-100%	5.9	600 cycles (0-50%)	Gao et al. ¹⁷
TPU	PANI	0-110%	17.15	unmentioned	Tian et al. ³¹
PLA and TPU	SWCNT	50-100%	33	unmentioned	Khalili et al. ³²
TPU	rGO	10-100%	79	6000 cycles (0-50%)	Wang et al. ³³
TPU	CNY	0-2%	1700	300 cycles (0-2%)	Yan et al. ³⁴
PA6 and PVA	CB	110-150%	9706.9	1000 cycles (0-10%)	Zhan et al. ³⁵
TPU	rGO and AgNWs	84-100%	4.4×10 ⁷	1000 cycles (0-10%)	Li et al. ³⁶
TPU	ACNTs and AgNPs	20-70%	1.04×10 ⁵	1000 cycles (0-70%)	Lin et al. ³⁷
TPU	AgNWs and ACNTs	38-100%	1.36×10 ⁵	1000 cycles (0-70%)	This work

Table 2.1 Comparison of the strain sensing performance for flexible strain sensors extracted from literatures and our work.

(TPU: Thermoplastic polyurethane; PLA: Polylactic acid; PA6: Polyamide 6; PVA: Polyvinyl alcohol; CNTs: Carbon nanotubes; PANI: Polyaniline; SWCNT: Single-walled carbon nanotube; rGO: Reduced graphene oxide; CNY: Carbon/graphene composites nanofiber yarn; CB: Carbon black; ACNTs: Acid modified carbon nanotubes; AgNPs: Silver nanoparticles; AgNWs: Silver nanowires)

Note: The Gauge factor (GF) (GF = $(\Delta R/R_0)/\epsilon$) is used to quantitatively evaluate the sensitivity of the strain sensor, and is calculated by the slope of the linear fitting curve.



Figure 2.16 (a) Schematic illustration of the sensing mechanism of the TPU/40-ACNTs/30-AgNWs/45-PDMS strain sensor. SEM images of the WCNCs during a complete stretching-releasing behavior, under the strain of (b and b') 0, (c and c') 30%, (d and d') 70%, (e and e') 100% and (f and f') 0.

In order to further study the sensing behavior of the WCNC strain sensor, a sensing mechanism is proposed, as shown in Figure 2.16a. The quasitwo-dimensional AgNWs layer of WCNC is a vital factor in the resistance change due to its sensitivity to large-scale stretching. Using the TPU/ACNTs porous nanofiber membrane as a template, through capillary action, surface tension, hydrogen bonding, and a small amount of Ag⁺ coordination, AgNWs can self-assemble into the pores and gaps of the TPU/ACNTs nanofiber membrane, and further form a compact hierarchical structure on the membrane surface (Figure 2.16b). Furthermore, the modification of PDMS also enhanced the interfacial interaction and the binding force of AgNWs. Under the strain of 30%, the TPU substrate undergoes slight elastic deformation, resulting in a small amount of microcracks on the outer AgNWs layer (Figure 2.16c). Due to the dense conductive network integrated by AgNWs, the deformation could only cause a slight increase in resistance. After further strain loading, AgNWs slipped slightly, resulting in an increase in overall resistance. Since the dense conductive network still has the ability to resist deformation, the increase of $\Delta R/R_0$ is relatively limited. However, larger strain of 70% breaks some parts of the entanglement structure of AgNWs, and more microcracks are generated in the quasi-twodimensional AgNWs layer, as shown in Figure 2.16d. As the microcracks expanding, $\Delta R/R_0$ increases significantly. In addition, due to the interactions of PDMS and AgNWs or AgNWs and TPU/ACNTs, the conductive layer is prevented from breaking to a certain extent, which helps to maintain the conductivity and retaining of the WCNC strain sensor. Therefore, when a large strain ($\varepsilon = 100\%$) is applied, the AgNWs layer still be further deformed and cracked, leading to a loosely structure, but not broken, as shown in the SEM images of Figure 2.16e and e'.

When the WCNC releases back to its original state, the outer quasi-twodimensional AgNWs layer automatically repairs the fractures and the AgNWs get entangled up again, restoring the original conductive network (**Figure 2.16f**). Different from the commonly used spraying method to modify one-dimensional and two-dimensional conductive nanofillers, the quasi-two-dimensional conductive network we constructed is based on the self-assembly and densely packed AgNWs. Although the AgNWs layer is formed on the surface of the WCNC, it does not exist independently outside. Because there still exists a large amount of AgNWs entangled and piled together inside the gaps of TPU/ACNTs, the externally mechanical action of WCNC can effectively realize the stress transfer to the outer layer, leading the outer AgNWs layer to undergo the stress and achieve superior sensing response.



Figure 2.17 The corresponding state of one single red LED with the WCNC as the connector under different strains. (a) Original state: $\varepsilon=0$, (b) Stretching: $\varepsilon=50\%$ and (c) Releasing: $\varepsilon=0$.



Figure 2.18 (a) Schematic diagram illustrating the WCNC in monitoring mode for body motions. Monitoring of numerous body motions by transient resistance change (R/R_0) using the WCNC as WSS: (b-d) Elbow movements with different bending degrees (45°, 90°, and 135°). (e) Neck movement. (f) and (g) show the motions of walking and knee squatting. (h) Finger movement with water dropping. (i) Vocal cord movement (speaking "SNU"). (j) Pulse rate. (The insets reflect the various positions of human body where the WCNC is attached to detect the body motions.)

The red LED circuit is constructed as another certification, in which WCNC is connected to the LED by wires, and a battery (AA, UM-3) is used as the power source. Obviously, when WCNC is in its original state, the red LED is lit (**Figure 2.17a**). When a parallel stretching force is applied to both sides of the WCNC, the LED gradually darkens, and the brightness disappears when the strain increases to about 50%, due to the outer AgNWs layer network exists more cracks (**Figure 2.17b**). Further, when we slowly remove the parallel stretching force on both ends of WCNC, WCNC gradually return to its original state because of its excellent resilience. Meanwhile, the conductive network repaired itself and the LED brightened again (**Figure 2.17c**). Since the matrix material has outstanding flexibility and resilience, and the conductive networks have excellent self-repairing property, WCNC is endowed with promising potential in the field of flexible electronics.

Here, WCNC is adhered to different positions of the human skin to monitor its corresponding movements, as shown in **Figure 2.18a**. Further, **Figure 2.18b-d** illustrate the R/R_0 of the WCNC strain sensor behavior when monitoring the movements of the elbow, the R_I is 1.7, 2.5 and 3.0, when the elbow bending angles are 45°, 90° and 135°, respectively. As the bending degree becomes larger, the generated deformation increases, which causes serious damages to the AgNWs layer network, resulting in higher R_I . **Figure 2.18e** shows the detection signal R_I reflected by WCNC is 2.8 when a nodding movement is performed. In addition, as shown in **Figure 2.18f-h**, other large body movements are also detected, such as leg movements (walking and knee bending) and finger bending. Interestingly, the sensor signals have not been disturbed upon monitoring the bending movement of finger, after applying the external interference (continuous dropping water onto the
working WCNC sensor). Because the superhydrophobic surface has a strong repulsion for water droplets and protects the internal conductive networks from interference, WCNC can work under some harsh conditions such as rainy and humid environments. In addition to detecting large body movements, WCNC is also very sensitive to some subtle body movements. It is used to monitor the vocalization of the human throat and the pulse rate, which also exist obvious responses, despite their R_I are much lower (Figure 2.18i and j). Outstanding flexibility, sensitivity, reliability, stability and durability endow WCNC as a promising potential for wearable strain sensors.



Figure 2.19 (a-d) Description of the skin affinity between the WCNC and human skin. No residual was left and no skin was hurt after the WCNC was peeled off (24 h). Photographs of a WCNC strain sensor on the wrist (e) before bending and (f) during bending. (g) Transient resistance change (R/R_0) of the WCNC strain sensor in two dimensions (the longitudinal (y₁-axis) and transverse (y₂-axis) directions).

Furthermore, our WCNC uses biocompatible PDMS as a protective layer, hence it has an excellent affinity to human skin, as shown in Figure 2.19a-d. However, most of the CPCs strain sensors, due to the limited composite structural characteristics, usually only perform onedimensional monitoring of human motions, which inevitably lead to the incomplete and imprecise monitoring results. Since our WCNC fully combines the advantages of quasi-two-dimensional AgNWs layer network and one-dimensional ACNTs network, it can realize simultaneous, and highly sensitive sensor monitoring in multiple vertical directions. Figure 2.19e and f illustrate that the WCNC strain sensor monitors the bending of the wrist in two vertical directions. Since the deformation of the wrist skin is mainly along the y_1 axis, the sensing signals are obvious, and the $R_{\rm I}$ can reach about 1.8. In addition to the y_1 axis, some detectable signals are also appeared on the y_2 axis, which illustrate the small deformation (Figure 2.19g). The WCNC can precisely monitor the body motions, which is quite important for the medical healthcare, particularly for old people and the patients who suffer the joint injuries, Parkinson's disease and other motion disorders.



Figure 2.20 The WST value of L929 cells and HSF cells under two different conditions (Control: in medium; Immersion: in extract substrate).



Figure 2.21 The microscopic images of L929 cells cultured for 24 h (a) in medium, (b) in extract substrate. The microscopic images of HSF cells cultured for 24 h (c) in medium, (d) in extract substrate.

As shown in **Figure 2.20**, the water-soluble tetrazolium (WST) is used for quantitative detection of the number of living L929 and HSF cells under two culture environments, namely, proliferation. We set purple samples (blank samples cultured in medium) as the optimal culture state, i.e., the total amount of 100%. The survival rate of cells in the other group is measured by the ratio of the number of cells in the culture system to the number of cells in the blank sample. We find that the survival rate of mouse fibroblast L929 cells cultured in WCNC extract for 24 h is about 85%, indicating that the exudate in WCNC extract has a certain inhibitory effect on the growth of L929 cells. On the contrary, for human skin fibroblast HSF cells, we can find that the survival rate reached more than 99% after 24 h culture in the extract of WCNC, indicating that WCNC would not exude toxic substances to harm human fibroblast.

Furthermore, the live/dead cell staining experiment of mouse fibroblast L929 cells has been put forward. Figure 2.21a and b are enlarging of the corresponding parts of Figure 2.21a' and b'. Obviously, L929 cells exist a flat oval shape, and the number of L929 cells surviving in the extract is reduced compared with that in the blank medium, which is consistent with the WST results. Figure 2.21c and d show the live/dead cell staining experiment of human skin fibroblast HSF cells, which are the magnification of Figure 2.21c' and d'. The overall staining is basically consistent with the data in WST. HSF cells are fusiform in blank samples containing only medium and in the extracts of WCNC, with uniform distribution and normal morphology. Therefore, WCNC has no influence or interference on cell morphology.

The data of WST and the results of live/dead cell staining experiment illustrate that WCNC has no cytotoxic substances exude from the extract,

so it is a non-toxic composite material to human epidermal tissue cells.

2.4 Conclusion

The WCNC (TPU/ACNTs/AgNWs/PDMS) strain sensor consists of highly elastic TPU as the matrix, then the one-dimensional ACNTs network and the quasi-two-dimensional AgNWs layer network are assembled on the surfaces of TPU nanofibers and TPU/ACNTs nanofiber membrane in sequence. Finally, PDMS is introduced into WCNC, playing a role in protecting and fixing the AgNWs layer, and endows WCNC with great superhydrophobicity, self-cleaning ability and anticorrosive resistance. Due to the synergy of the different dimensional conductive networks, the conductivity of WCNC is as high as 3506.8 S/m, leading WCNC to possess superior strain sensing performance. The GF of WCNC is as high as 1.36×10^5 , and it also exhibit a quite large working strain (from 38% to 100%). During the process of strain sensing, even cycled for more than 1200 times under the strain of 70%, WCNC still maintains good stability and durability. WCNC strain sensor can monitor a variety of human joint movements even under harsh environments, and realize the simultaneous and more precise body motion monitoring in multiple vertical directions.

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Chapter 3. An In-situ Self-assembly Dual Conductive Shell Nanofiber Strain Sensor with Superior Sensitivity and Antibacterial Property

3.1 Motivation

Stretchable, flexible and wearable electronic devices have been widely used due to their light weight, easy adhesion to skin and the ability to withstand mechanical deformation.¹⁻³ Especially in the aspect of biosensors for medical healthcare, it has become an important device for monitoring biological signals,^{3, 4} such as heart rate and blood pressure.^{5,} ⁶ Flexible electronic devices are mainly based on flexible materials, combined with micro-nano processing and integration technology.⁷⁻⁹ To design and manufacture of a new generation of flexible electronic devices that can realize logic amplification,¹⁰ filtering,¹¹ data storage,¹² signal inversion,¹³ digital operation,¹⁴ sensing and other functions is an urgent request for the development of information technology and modern medical.¹⁵ Flexible functional materials have unique physical and chemical properties such as optical, electrical, magnetic, thermal and mechanical properties, which make flexible electronic devices can be widely used in flexible display, data encryption, wearable sensing and other intelligent electronic systems.^{16, 17} Generally, the performance and use of the flexible strain sensors are largely determined by the properties of the basic substrates. Among them, one-dimensional fiber and yarn can be prepared by spinning and wrapping.¹⁸ They can meet the sensing test in the strain direction, but they are usually used to detect small deformation due to the weak mechanical properties.¹⁹ After spin coating and electrostatic spinning are used to construct two-dimensional flexible films, the mechanical properties of the substrate materials are further

improved, and simultaneity of strain monitoring can be realized in the plane dimension.²⁰ In addition, three-dimensional foam, aerogel and other substrate materials provide a new idea for pressure sensor, realizing the strain monitoring in the longitudinal dimension.²¹

Conductive polymer composites (CPCs) are ideal substrates for strain sensors because of their controllable conductivity, light weight, modifiable properties and easy manufacture.²²⁻²⁴ However, most CPCs possess large thickness and solid structure, so there exists some instability in the preparation process, such as uneven dispersion of conductive fillers and obvious difference in mechanical strength of different CPC parts.²⁵⁻²⁷ In addition, most CPCs have poor air permeability due to very few interspaces in their polymer substrates, which leads to their weak skin affinity.²⁸ In order to solve the above problems, electrospinning technology is introduced into the preparation of strain sensor substrates.²⁹ Furthermore, conductive nanofiber composites (CNCs) have been extensively studied for their flexibility,³⁰ skin affinity,³¹ air permeability,³² porous structure,³³ and large aspect ratio.³⁴ In previous studies, CNCs were produced by electrospinning polymer solutions which are doped with the conductive nanofillers.³⁵ The method limits the conductive effect of the nanofillers, because conductive nanofillers tend to accumulate at the inside of the nanofibers.³⁶ As an alternative, through in-situ reduction and selfassembly or the effect of external force, nanofillers can be uniformly decorated on the surfaces of the nanofiber or membrane.³⁷ Generally, these conductive nano-networks modified on the surface are unstable and easy to fall off. In our former research, we put forward the ultrasonication to induce adsorption of ACNT to form a one-dimensional conductive network layer on TPU nanofibers, utilize capillary action to selfassemble a quasi-two-dimensional AgNWs layer conductive network, and further establish an outer protective layer, modifying PDMS to prevent nano conductive network from falling off and damaging, which may occur during the stretching and contacting process.²⁸ Additionally, we also put forward a facile preparation process to build the TPU/ACNTs/AgNPs/PDMS conductive nanofiber composites, which also introduced the PDMS glue to protect the dual conductive networks.³⁸ Actually, these two CNCs are praised for conductivity, superhydrophobicity, and strain sensing performance, but we are now considering how to simplify the former preparation procedures and largely improve the stability of the outer conductive network.

In this study, we continue to use acid modified carbon nanotubes (ACNT), which are easily to anchor through strong ultrasonication. Subsequently, a preliminary one-dimensional ACNT conductive network is formed on the TPU nanofibers surface, which has a large amount of active functional groups, such as -OH, -COOH. Based on this, we propose a new method of in-situ modification and self-assembly to form silver nanoflowers (AgNF). With the increase modification times of insitu self-assembly reductions, AgNF gradually grow on the surface of the nanofibers, and the AgNF petals are connected to each other to form a dense AgNF shell conductive network. M-CNC exhibits extremely high electrical conductivity (up to 7.5×10^5 S/m) due to the synergistic effect of two dual shell conductive networks of different dimensions (ACNT and AgNF). The electrical conductivity and surface conductive network structure of the M-CNC show superior stability even after multiple stretch-release cycles (up to 1000 times at 50% strain). Furthermore, the double-shell conductive networks endow M-CNC with outstanding sensing performance, possessing a large gauge factor of 55352 with the

working strain ranging from 42% to 100%. M-CNC strain sensor can realize accurate human motion monitoring in multiple directions simultaneously on the same horizontal plane. In bacterial environments, AgNF endow the M-CNC with great antibacterial property, indicating brilliant growth inhibition effects on Gram-negative Pseudomonas aeruginosa (P. aureus, ATCC 27853) and Gram-positive Staphylococcus aureus (S. aureus, ATCC 25923).

3.2 Experimental section

3.2.1 Materials and chemicals

Nitric acid (HNO₃, 65-68%), sulfuric acid (H₂SO₄, 65-98%), N, Ndimethylformamide (DMF), tetrahydrofuran (THF), silver nitrate, concentrated ammonia, L-ascorbic acid and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. Thermoplastic polyurethanes (TPU) were bought from Ningbo Kingsui Rubber Plastic Co. Ltd. Multi-walled carbon nanotubes (MWCNTs) were purchased from Nanjing XFNANO Materials Tech Co. Ltd. (diameter: 10-20 nm, length: 10-30 µm).

3.2.2 Preparation of TPU substrate

The TPU particles were dissolved in the mixture of DMF/THF (the volume ratio of DMF to THF was 3:1) and magnetically stirred at 70 °C for 12 h to obtain a uniform TPU solution with the concentration of 20 wt%. The prepared TPU solution was transferred to a 10 mL syringe with a metal needle for electrospinning. The spinning parameters were as follows: the voltage was 18 kV, the distance was 12 cm, the speed of the push column was 2 mL/h, and a layer of aluminum foil was attached to the rotating drum to collect the TPU nanofiber membrane. The finally obtained TPU nanofiber membrane is white and slightly yellow, which is easy to peel from the peeling aluminum foil paper.

3.2.3 Acid modification of CNTs

Firstly, we added 40 mL of concentrated sulfuric acid and nitric acid (the volume ratio of concentrated sulfuric acid to concentrated nitric acid is 3:1) to a 100 mL three-mouth flask. After that, 500 mg of multi-walled carbon nanotubes (MCNTs) were added to the flask. In order to get uniform dispersion, the mixed solution undergo ultrasonic processing for 30 min. Under the temperature of 60 °C, we let the dispersion maintain magnetic mixing acid and reflux 4 h. After repeated centrifugation, filtration, and a large amount of deionized water washing to neutral and drying, acid modified carbon nanotubes (ACNT) were finally obtained.

3.2.4 Preparation of TPU/ACNT

The ACNT were first added into the mixture of ethanol and deionized water (the volume ratio of deionized water and ethanol was 1:1), and then the ACNT dispersion was obtained by ultrasonic for 20 min. The TPU nanofiber membrane was immersed into the ACNT dispersion and the ultrasonication process was carried out for different times. During the process of ultrasonic adsorption, ACNT was gradually fixed on the surface of the softened TPU nanofibers. Finally, the obtained TPU nanofiber composite was washed with a mixture of alcohol and water to remove residue, and dried in the oven to obtain TPU/ACNT-X nanofiber composite, of which X represents the ultrasonic time.

3.2.5 Preparation of TPU/ACNT/AgNF nanofiber composites

The silver nitrate solution (1 mol/L) and potassium citrate solution (0.5 mol/L) were stirred at 50 °C for 2 min to form a white silver citrate complex. Ammonia water was added until the solution became limpid, and then boric acid solution (0.5 mol/L) was added to the silver precursor

solution. First, TPU/ACNT was immersed in L-ascorbic acid solution (0.3 mol/L) for 15 min, then it was dried in a 60 °C oven for 5 min, and then immersed in silver precursor solution for 15 min. Finally, it was rinsed with deionized water and put into the oven for drying. TPU/ACNT-X/AgNF-Y nanofiber membrane composites with different AgNF content were obtained by the number of repeated reductions, where Y represents the number of cycles.

3.2.6 Characterization

The microscope (Nikon ECLIPSE, LV100) and the field emission scanning electron microscopy (FESEM, Hitachi S-4800) were used to characterize the microstructure of samples and its composites. Energy dispersive X-ray (EDX) spectra were used to observe the element distribution in the cross section of brittle fracture samples, and the shell structure was revealed. X-ray diffraction (XRD, Bruker D8 Advance with Cu K α radiation λ =0.15406 nm) was used to analyze the diffraction intensity of the samples. Fourier transform infrared (FT-IR) spectroscopy (Alpha, Bruker, Karlsruhe, Germany) verified the physic-chemical composition of the sample. Thermogravimetric analysis (TGA, Mettler Toledo) is used to determine the degree of thermal decomposition and component content in TPU/ACNT/AgNF. An Instron Mechanical Tester (model 3367) was chosen to determine the mechanical properties of the nanofiber composites under the test rate of 50 mm·min⁻¹.

3.2.7 Conductivity measurement

Surface resistance and resistivity of different M-CNCs was carried out by four-probe resistance tester (RST-9). The conductivity was finally determined by averaging the results on 5 different positions.

3.2.8 Strain sensing performance measurement

The strain sensitivity is the most important evaluation criterion of the

strain sensor. To avoid possible errors in unsteady state conditions, M-CNC samples were pre-stretched 20 times before the sensing signal was recorded. M-CNC samples were assembled into sensors using conductive silver paste and copper wire and fixed with conductive adhesive. The M-CNC is connected to a resistance meter (DMM4040) for real-time monitoring of resistance changes during the stretch-release process. Transient resistance and initial resistance, represented by *R* and *R*₀ respectively, are important parameters of reaction sensing capability. ΔR represents the change of resistance, and the response value of the strain sensor is expressed by *R*/*R*₀. In general, the concept of strain sensor sensitivity is defined as the strain gauge factor (GF), and its calculation formula is GF= ($\Delta R/R_0$)/ $\Delta \varepsilon$, where $\Delta \varepsilon$ is the actual working strain.

3.2.9 Antibacterial test

In order to investigate the antibacterial properties of M-CNC, we used the method of constructing antibacterial ring on solid porous gel plate. Gram-negative Pseudomonas aeruginosa (ATCC 27853) and Grampositive Staphylococcus aureus (ATCC 25923) were used as the experimental flora. First, the bacterial suspension was oscillated in an incubator at 37 °C for 12 h. Then, a double-layer AGAR medium was prepared, and 20 mL fused LB AGAR medium was spread on the bottom layer of a culture dish with a diameter of 90 mm. After cooling, a certain volume of bacterial suspension was added to the LB AGAR medium at about 50 °C to spread evenly. In the upper bacterial medium, the microbial density on 1 mL forming unit was about 10⁸-10⁹ colonyforming units (CFU). When the plate was hardened, circular thin films of TPU/ACNT (as control group) and TPU/ACNT/AgNF composites were placed on the surface (diameter was 6 mm; each group has three samples). After incubation at 37 °C for 24 h, the antibacterial zone was observed.

3.3 Results and discussion

The TPU nanofiber membrane are served as the substrate for the multifunctional conductive nanofiber composite (M-CNC), decorated with acid modified carbon nanotubes (ACNT), and in-situ selfassembled silver nanoflowers (AgNF), entitling the M-CNC with dual shell conductive networks (Figure 3.1a). The M-CNC exhibits great flexibility because the TPU nanofiber membrane is flexible and bendable, so the M-CNC fully inherits these advantages as well (Figure 3.1b). The thickness of the M-CNC membrane is about 0.224 mm (Figure 3.1c), and the dual shell conductive networks offer the M-CNC an initial resistance of 2.92 Ω (Figure 3.1d). As illustrated in the cross-sectional image of a single nanofiber of M-CNC (Figure 3.1e), AgNF are tightly wrapped around the outside of TPU/ACNT nanofiber, forming an obvious shell structure with a thickness of about 250 nm. According to the SEM and TEM images (Figure 3.2a and b), Ag element cluster together to form the structure of AgNF, and the diameter of a single AgNF is about 600 nm. The crystal structure and diffraction pattern of AgNF are characterized by XRD in Figure 3.2c, which illustrates the characteristic peak position and strength of Ag. The mapping image shows the distribution trend of multiple units (Figure 3.1f-i). It can be seen that three elements of carbon, oxygen and nitrogen, as the main components of TPU/ACNT, are uniformly distributed in the interior of the nanofibers, while Ag is largely distributed in the periphery. Although AgNF is wrapped around the outer surface of TPU/ACNT nanofibers by in-situ self-assembly method, it has a quite firm shell structure. As shown in the Figure 3.2d, after the ultra-low temperature of liquid N₂, the M-CNC was brittlely broken, and we found that even if the TPU nanofibers

are shed, the AgNF can still maintain the original shell structure. In other words, TPU nanofiber is served as a template for forming the AgNF shell structure. The rigid ACNT with high surface energy are easily anchored on the surface of TPU nanofibers through the force of ultrasonic waves, which are smooth and viscoelastic. The acidified groups of ACNT play quite important roles to enhance the combinations between TPU and ACNT, which can be attributed to the hydrogen bonds. Further, from **Figure 3.3a-c**, when the ultrasonication time is less than 30 min, there exist only a small amount of ACNT decorated on the TPU nanofibers surfaces (**Figure 3.3d-f**). Gradually, with the increase of ultrasonic time X, the TPU nanofibers are almost coated with ACNT. Especially when the ultrasonic time X comes to 50 minutes, the conductivity of TPU/ACNT reaches the highest value of 5.70 S/m, and then shows a stable trend (**Figure 3.4**).



Figure 3.1 (a) Schematic diagrams of the M-CNCs components and its applications for body motion monitoring and antibacterial. (b) The bent M-CNC membrane exhibiting flexibility. (c) Thickness of M-CNC membrane. (d) Resistance of M-CNC membrane. (e) SEM image of the cross-sectional structure of single nanofiber of M-CNC. (f-i) EDX illustrating elemental mapping images of C, N, Ag, and O.



Figure 3.2 (a) SEM and (b) TEM images of the AgNF. (c) XRD analysis of AgNF. (d) The AgNF tubular structure was left after the internal TPU template was removed by the frozen brittle.



Figure 3.3 SEM images of the TPU/ACNT-X (different modification time of ACNT). X: (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min, (e) 50 min and (f) 60 min.



Figure 3.4 Conductivity of TPU/ACNT-X, X represents the different modification time.

As mentioned above, Ag citrate complex is used as the precursor, and TPU/ACNT membranes loaded with in L-ascorbic acid solution are immersed in the precursor solution for several times, and the number of repeats is recorded as Y. From Figure 3.5a-f, with the increase of repetition times Y, it is not difficult to find that the surface of TPU/ACNT nanofibers gradually begins to be modified by AgNF. When Y comes to 5, a large number of AgNF aggregates in the gap between TPU/ACNT/AgNF nanofibers. To some extent, the agglomerated stacking may increase the overall conductivity of M-CNCs (Figure 3.6), but it also causes instability in conductivity changes during strain sensing applications, especially after large strain and cyclic tests. As shown in Figure 3.7a-c, when the number of in-situ modification is less than 4 times, the surface of M-CNCs nanofiber only exists a small area of selfassembled AgNF. In contrast, after more times of repeated modification, the unique shell structure of AgNF gradually forms (Figure 3.7d-f). Please note that the final obtained M-CNC is TPU/ACNT-50/AgNF-4.



Figure 3.5 SEM images of the modified nanofibers morphologies of M-CNCs with different AgNF modification cycle numbers at the scale of 10 μ m. Y: (a) one time, (b) two times, (c) three times, (d) four times, (e) five times and (f) six times.



Figure 3.6 Conductivity of TPU/ACNT-50/AgNF-Y, Y represents the different modification number.



Figure 3.7 Scanning electron microscope images of the finally obtained M-CNCs nanofibers morphologies with different AgNF modification cycle numbers at the scale of 50 nm. Y: (a) one time, (b) two times, (c) three times, (d) four times, (e) five times, (f) six times.

The crystal structure of the processed material is characterized by the XRD pattern in Figure 3.8a. The XRD patterns of TPU/ACNT show almost smooth waveforms, and there are almost no obvious characteristic peaks. In the diffraction range of 16° to 23°, pure TPU has a wide diffraction peak band, but this situation disappears with the modification of ACNT and AgNF. After the introduction of AGNF, the XRD patterns of M-CNC show four sharp diffraction peaks at 38.3°, 44.5°, 64.7° and 77.5°. The peaks are high and narrow, which were attributed to the four crystal planes of AgNF, namely 111, 200, 220 and 311, indicating that the great crystallinity of AgNF.³⁹ Functional groups of M-CNCs nanofibers and their composites as well as the interactions between multiple components is characterized by FTIR. As shown in Figure 3.8b, TPU nanofiber membrane is composed of polycarboxates, which is rich in N-H and C-O-C groups. As a result, the corresponding peaks located at 3332 cm⁻¹ and 1072 cm⁻¹ are generated on FTIR spectrum. Compared with the two more concentrated absorption peaks, the ones located at 1726 cm⁻¹ and 1529 cm⁻¹ belong to the -H-N-COOgroup.⁴⁰ Because ACNT are rich in -OH and -COOH groups, after ACNT modification, the peaks exist some slight shift, from1726 cm⁻¹ and 1529 cm⁻¹ to 1725 cm⁻¹ and 1528 cm⁻¹.⁴¹ The result indicates that there are some interfacial interactions between TPU and ACNT, such as hydrogen bonding.⁴²

The components of M-CNCs were further explored by thermogravimetric analysis (TGA). The TGA curve is shown in **Figure 3.8c**. After thermal degradation of TPU, TPU/ACNT-50 and TPU/ACNT-50/AgNF-4 at 800 °C, the residual weight percentages were 6.78%, 8.21% and 47.65%, respectively. We make a difference in the statistical results to further analyze each component, which reveal that

the weight percentage of AgNF in final M-CNC (TPU/ACNT-50/AgNF-4) is approximately 39.44%. Although rigid ACNT and AgNF were assembled on the TPU nanofiber membranes successively, the elongation at break of the three TPU and its composites remained almost unchanged. It is worth noting that the tensile strength of TPU/ACNT/AgNF shows a significant improvement at the strain of 0-400%, which is accounting for the enhanced mechanical properties of the AgNF shell structure formed by the self-assembly of the outer layer under small strain. After that, due to the complete cracking of the AgNF shell, the high elasticity of the TPU substrate is still existed under large strain (**Figure 3.8d**).



Figure 3.8 (a) XRD analysis and (b) FT-IR spectra for TPU, TPU/ ACNT-50 and TPU/ACNT-50/AgNF-4. (c) TGA and (d) Typical stressstrain curves of TPU, TPU/ACNT-50 and TPU/ACNT-50/AgNF-4.

Usually in practical applications, especially human body motion monitoring, signal transmission under small strains is extremely important, reflecting the minimum detection limit of M-CNC. Figure 3.9 is the periodic signals generated when M-CNCs carry out some small strains. From the variation of signals, it can be found that the variation of response factor (R_I : maximum R/R_0) is positively correlated with the variation of tensile displacement, which are 0.0065, 0.0155, 0.085, 0.193, 0.638 and 5.42, at the strain of 0.5%, 1%, 3%, 5%, 10% and 20%, respectively. When the strain increases, there has been a leap in the $R_{\rm L}$ Since the strain reaches 20%, the $R_{\rm I}$ has increased almost tenfold with every 20% increase in strain, from 250 at $\varepsilon = 40\%$ to 3×10^4 at $\varepsilon = 100\%$ (Figure 3.10a-d). Large resistance variation under large tensile strain ensures extensively high sensitivity of M-CNCs. Since the zerodimensional AgNF shell conductive network has good stability, coupled with the internal one-dimensional ACNT conductive layer maintains the conductive pathway, M-CNCs have good strain sensing stability and good reproducing output signals (Figure 3.10e). As shown in the insets, we have selected the front and last two parts in 1000 cycles (cycling test time more than 1×10^4 s) respectively, which are quite stable and detectable, illustrating outstanding stability.



Figure 3.9 Resistance variations of the M-CNCs under (a) $\varepsilon = 0.5\%$, (b) $\varepsilon = 1\%$, (c) $\varepsilon = 3\%$, (d) $\varepsilon = 5\%$, (e) $\varepsilon = 10\%$ and (f) $\varepsilon = 20\%$ (strain rate: 50 mm·min⁻¹).



Figure 3.10 (a-d) Resistance variations of the M-CNCs under ε = 40%, 60%, 80% and 100% (strain rate: 50 mm·min⁻¹). (e) M-CNC based strain sensor under 50% strain for long-term sensing stability of 1000 times cycle test.

As can be seen from Figure 3.11a, when M-CNC rapidly reaches 30% strain (strain rate: 1500 mm·min⁻¹), the resistance response time of M-CNC is 115 ms and the resistance recovery time is 76 ms. Rapid response and recovery times endow the M-CNC with the ability to rapidly and continuously monitor subtle movements. We subjected M-CNC to five strain stretching and releasing rates (30, 50, 80, 120, and 200 mm/min) to further analyze the stability of its strain sensing. The results show that no matter in low speed or high-speed test state, M-CNC can output signal stably and clearly (Figure 3.11b). As shown in Figure 3.11c, when ε is between 0 and 42%, the resistance change increases linearly at low speed. This indicates that the compact AgNF shell structures are stacked together, which is enabled for the integrity of conductive network. Although M-CNC is deformed by stress transmission, the dense AgNF structure can effectively resist a certain small strain, so that the conductive network will not cause significant damage, so we calculated that GF is 855. The high GF at small strains ensures that M-CNC can be used for monitoring micro-motions. In a large strain range ($42\% < \varepsilon <$ 100%), the AgNF shell structure cannot be maintained and is seriously damaged. The resistance of M-CNC increases linearly and rapidly. However, due to the strain insensitivity of the internal one-dimensional ACNT network, the resistance of M-CNC is still detectable even after experiencing large strain and the damage of the outer conductive network. Finally, GF was calculated as 55352. Same as many other nanofiberbased strain sensors, M-CNC has a similar GF variation pattern.



Figure 3.11 (a) Instant response and recovery time of the M-CNC under a strain of 30% with the stretching rate of 1500 mm·min⁻¹. (b) The strain sensing performances of the M-CNC at different tensile speeds (30, 50, 80, 120 and 200 mm·min⁻¹) under the strain of 50%. (c) Two linear fitting curve (0% < ϵ < 42% and 42% < ϵ < 100%).
In order to explore the variation of M-CNC with dual conductive shell networks during stretching process, we have deeply studied the surface morphologies, and further revealed the strain sensing mechanism. As shown in Figure 3.12a, the in-situ self-assembled zero-dimensional AgNF shell conductive network only exists small changes under the small strain of 10%. In other words, the overall conductive networks are almost complete, producing a small change in resistance. However, as the strain gradually increases, some visible cracks and gaps appear on the outer AgNF shell layer, leading to the resistance of M-CNC begins to increase considerably, as shown in Figure 3.12b. Because under small strains, the AgNF structure stacked on the outer layer of M-CNC nanofiber would not appear very obvious cracks. Because the nanoflowers that are open like petals, and can still contact each other when the AgNF individuals are separated to a certain extent, maintaining the original AgNF conductive network. As mentioned in Figure 3.11c, GF takes a great leap change when the strain larger than 42%. Furthermore, when the tensile ratios are 70% and 100% (Figure 3.12c and d), it could be seen from the SEM images that the crack size and density of M-CNCs are gradually enlarged, which reveals that the conductive AgNF shell network separated greatly, leading to the continuous and large enhancement of $R_{\rm I}$. On account of the entangled ACNT conductive network possesses insensitivity to the strain, the M-CNCs are still conductive even at the strain of 100%. Additionally, due to the good resilience of TPU nanofibers, the firm AgNF is close to each other during the releasing process, and due to the stable in-situ selfassembly structure, the conductive network can be basically restored when it returns to the original position.



Figure 3.12 SEM images of M-CNCs at different strain during stretching. (a) ε =10%, (b) ε =30%, (c) ε =70%, and (d) ε =100%.

As mentioned above, signal transmission under small strains is extremely vital for the quality of body motion monitoring of M-CNCs. First of all, we use M-CNC to monitor the very minute pulsation and find that the M-CNC could reliably output a signal wave of $\Delta R/R_0=0.05$ (Figure 3.13a). In addition, the M-CNC is placed on the throat for movement monitoring of swallowing, with two steady signal spikes $(\Delta R/R_0=0.45)$ occurring after each swallowing (Figure 3.13b). As we all know, a simultaneous, and highly sensitive strain sensor that can monitor the body motions in multiple vertical directions is effective to avoid many errors and mistakes brought by the process of monitoring. Notably, the M-CNC can meet the requirements, which is used to test the motion of fist, wrist, finger and knee, as shown in Figure 3.13c-f. Since large changes in body movements are usually in the direction perpendicular to where the human body is, the body motion signals are quite obvious along the y₁ axis, and the $\Delta R/R_0$ can reach about 0.7, 17.5, 24 and 137 for the fist, wrist, finger and knee, respectively. In addition, in the same part of the body, the skin deformation exists in multiple horizontal directions, and the realization of simultaneous monitoring of multidirection body movements in the same part could greatly improve the accuracy of body motion monitoring. M-CNC can also detect small deformation signals in the direction of y_2 axis perpendicular to y_1 axis.



Figure 3.13 M-CNCs serve as wearable strain sensors for accurate body motion monitoring: (a) pulse rate, (b) swallowing. The $\Delta R/R_0$ of the M-CNC strain sensor in the longitudinal and transverse directions (y₁-axis and y₂-axis): (c) fist movement, (d) wrist movement, (e) finger movement and (f) knee bend.

Furthermore, we attach M-CNC to human skin for 24 hours, then peel it off, and find that there are no obvious skin adverse reactions or residues on the skin where the M-CNC was attached (Figure 3.14a-d). We have further tested the Contact Angle of M-CNC with two different liquid droplets (pH=4.2 and pH=7.5), as shown in Figure 3.15. M-CNC exhibits obvious hydrophobicity to the two kinds of droplets, which indicates the stability under sweat conditions. Wearable strain sensors are mostly in direct contact with human skins, when worn for a long time, sweat and body fluids would overflow from the pores of the skin, which could easily cause bacteria to breed on the sensors, leading to the occurrence of some skin diseases.^{43, 44} To overcome this obstacle, we set the antibacterial test for M-CNC, choosing two common trauma-causing bacteria as the experimental strains: Gram-negative Pseudomonas aeruginosa (P. Aureus, ATCC 27853) and Gram-positive Staphylococcus aureus (S. Aureus, ATCC 25923). TPU/ACNT is used as the standard sample group for the experiments. However, we are surprised to find that TPU/ACNT shows excellent antibacterial properties (with obvious inhibition zones) on both Pseudomonas aeruginosa and Staphylococcus aureus AGAR medium plates, with diameters of 12.00 ± 0.25 mm and 8.67 ± 0.41 mm, respectively (Figure 3.14e and f). This effect probably accounts for the bacteria coming into direct contact with the ACNT, and we speculate that the long and thin carbon nanotubes may have punctured the bacteria and caused their damages. The best antibacterial effect is undoubtedly TPU/ACNT/AgNF nanofiber membrane, because its surface is coated with a dense AgNF shell layer. When placed on the AGAR layer, AgNF will gradually release Ag⁺, which will bind to the sulfhydryl groups (-SH) of the protein in bacteria and firmly adsorb, making them inactivated and coagulated. Further, the Ag⁺ can destroy

the activity of some functional enzymes in bacteria, which makes the internal mechanism of microorganisms disordered and eventually leads to apoptosis.⁴⁵⁻⁴⁷ Therefore, TPU/ACNT/AgNF samples exhibited the best antibacterial effect, as shown in Figure 3.14g and h. The diameters of inhibition zones are 14.00 ± 0.04 mm (P. aureus) and 12.50 ± 0.17 mm (S. aureus), respectively. To further analyze the antibacterial activity of TPU/ACNT and M-CNC, bacterial inhibition rate was carried out, as shown in Figure 3.16. For bacterial inhibition rate tests, the antibacterial activity of the composites exhibited a positive correlation with the existence of Ag. The M-CNC loaded with AgNF exhibited high levels of antibacterial activity with a bacterial inhibition rate of 64.28% and 71.32% for P. aureus and S. aureus. However, the TPU/ACNT composites showed relatively weak antibacterial activity, indicating that AgNF confers the important antibacterial effect. The M-CNCs have excellent antibacterial biological function, which will expand the new idea of M-CNCs application in vitro to a large extent.



Figure 3.14 Skin affinity of M-CNC: (a) Bare limb skin, (b) Attaching the M-CNC to the skin, (c) Wrapping the M-CNC and limbs with a bandage, (d) Removing the bandage and M-CNC after 24 hours. The M-CNCs (6 mm in diameter) nanofiber membrane were placed on AGAR plate cultured with common trauma bacteria, and the antibacterial region was observed. The experimental floras are: (e) TPU/ACNT (Control, P. aureus), (f) TPU/ACNT (Control, S. aureus), (g) TPU/ACNT/AgNF (P. aureus) and (h) TPU/ACNT/AgNF (S. aureus).



Figure 3.15 The Contact Angle of M-CNC with two different liquid droplets: (a) pH=4.2 and (b) pH=7.5.



Figure 3.16 Bacterial inhibition rate of P. aureus and S. aureus in liquid medium containing different composites after 24 h of culture.

3.4 Conclusion

The M-CNCs (TPU/ACNT/AgNF) strain sensor exhibits unique dual shell structures, consisting of the basic elastic TPU substrate, the onedimensional ACNT conductive network and the zero-dimensional AgNF conductive network. TPU and its composite materials have great resilience and high elasticity after being stretched and compressed. The rigid ACNT and AgNF not only maintain the elongation at break of the composites almost unchanged, but also obviously improve the tensile strength of TPU/ACNT/AgNF at the strain of 0-400%. Additionally, the dual conductive networks endow the M-CNCs with great conductivity, strain sensing ability and antibacterial property. The conductivity of M-CNC (TPU/ACNT/AgNF) is up to 7.5×10^5 S/m. Further, the M-CNC strain sensor possess a large gauge factor of 55352 with the working strain ranging from 42% to 100%. The outer AgNF shell structure is stable even after the cyclic test for 1000 times under the strain of 50%. The AgNF also endow the M-CNCs with great antibacterial property, indicating brilliant growth inhibition effects on P. aureus and S. aureus.

3.5 Reference

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Chapter 4. Wearable and Antibacterial HPMCanchored Conductive Polymer Composite Strain Sensor with High Gauge Factors Under Small Strains

4.1 Motivation

Nowadays, traditional electronic strain sensors are mostly based on metal and semiconductor materials, which have quite poor portability,^{1,2} flexibility³ and wearable ability.⁴ With the rapid development of flexible electronic devices and sensing technology, the applications of flexible strain sensors in electronic skin and robots have attracted more and more attention.⁵⁻⁷ On account of a series of advantages such as biocompatibility,⁸ mechanical deformation resistance,⁹ skin affinity,¹⁰ wearable ability,¹¹ real-time monitoring¹² and non-invasive manner,¹³ the development of strain sensors with high elasticity and stretchability has gradually become a research hotspot.¹⁴⁻¹⁶ Especially in the aspect of biosensors, it has become an important device for monitoring biological signals related to health, such as heart rate and blood pressure.^{17, 18} Flexible electronic devices are the main forms of flexible electronics, among them, conductive polymer composites (CPCs), which are flexible, low cost and easily processed, have become the promising candidates for flexible strain sensors.¹⁹⁻²¹

In essence, the strain sensing mechanism is that when the CPC is subjected to external force, the conductive network is destroyed, leading to a rise in resistance, or when the strain is released, the conductive network would gradually recover and the resistance would return to its initial value.²² In general, the concept of CPC strain sensor sensitivity is defined as the strain gauge factor (GF), high GF means that the sensor

has better resolution and response to the deformation caused by external forces.²³ The traditional method of preparing CPCs is to directly mix conductive nanofillers, such as carbon nanotubes, graphene, and metal nanoparticles, into the polymer substrates through solution or melting treatments.²⁴ However, due to the high surface energy and easy aggregation of nanofillers, it is difficult to distribute evenly in the matrix, which will result in a negative impact on the mechanical strength and electrical conductivity of CPCs.^{25, 26} In addition, CPCs generally exhibit low conductivity, as most nanofillers are wrapped by polymers, which greatly impede electron transport, due to their insulating properties.^{25, 27} Hence, it is necessary to add a high concentration of conductive nanofillers to form a stable and conductive network with strong electron transport ability, but it will also cause the induced strain, nanofiller agglomerations and the reduction of mechanical strength of CPCs.²⁸ In order to effectively avoid the increase of seepage threshold and the decrease of conductivity, researchers have proposed the physically selective modification of conductive nanofillers on the surface of polymer particles or polymer substrates.²⁹ However, this structure leads to a decrease in mechanical strength, flexibility, and stretchability.^{30, 31} Despite its excellent conductivity, the pre-formed interface conductive network usually results in both small gauge factor and small working strain. Furthermore, the air permeability of traditional elastomer CPCs is limited.³² When they are used as wearable devices, it is unavoidable to contact the body fluid and sweat environment, and easy to exhibit bacteria breeding, leading to some skin diseases. If CPCs are endowed with antibacterial properties, their applicability and affinity for human body as wearable strain sensors can be greatly improved.^{33, 34} Actually, HPMC is a kind of biopolymer that is biodegradable, environmentally

friendly, and bio-friendly and is used as thickener, dispersant, binder, excipient, emulsifier and stabilizer in textile industry.³⁵ It is also widely used in synthetic resin, petrochemical, ceramics, paper, leather, medicine, food, cosmetics and others. In the current studies, most researchers have mixed polymer substrates with HPMC to improve the surface adhesion or just used HPMC as the dispersant for conductive nanofillers, but there are few reports on the method of fixing conductive nanofillers by HPMC conjunctiva on the surface of polymer substrate.³⁶ After the formation of HPMC conjunctiva, mechanical properties of most composites are almost the same as those of the original substrates, and the ordinary elastic polymers can be bonded by strong hydrogen bond interactions with HPMC.^{37, 38}

The purpose of this paper is to propose a new way that can greatly improve the bonding effect of conductive nanofillers and flexible polymer substrates in the case of selective surface modifications, thereby greatly enhancing the performance of CPCs as strain sensors. In this paper, we innovatively put forward the traditional casting method to first prepare the AgNF embedded and dispersed by HPMC into a micronscale film conductive network, and then cast TPU on the upper part of HPMC/AgNF to obtain the TPU/HPMC/AgNF (M-CPC). Due to the formation of hydrogen bond interactions between TPU and HPMC, the AgNF dispersed by HPMC can be very firmly modified on the surface of TPU, thus owning excellent conductivity, strain sensing performance and cyclic stability. As a comparison, we also propose the physically selective surface modification to directly modify the AgNF conductive film on the TPU elastic substrate in the molten state, and the related performance data has been further analyzed. However, TPU/AgNF exhibits very poor performances both in the stability of external AgNF

networks and in the reliability of cyclic tests. Furthermore, the M-CPC possesses a high conductivity about 198 S/cm and extremely stable sensing signal output that can be monitored cyclically (more than 500 stretching-releasing cycles). Additionally, the HPMC dispersed AgNF conductive network endows the M-CPC with superior strain sensing performance, possessing a high GF of 2.8×10⁷ during the working strain from 30% to 35%, which is the highest GF of CPCs under small strains and has never been reported before. It is worth noting that both TPU/AgNF and M-CPCs are endowed with outstanding antibacterial properties due to the existence of AgNF. However, due to the slow dissolution of HPMC in the bacterial growth environment, the HPMC dispersed and embedded AgNF can be released slowly along with the dissolution of HPMC, which has a relatively long-term antibacterial effect, comparing with TPU/AgNF.

4.2Experimental section

4.2.1 Materials and chemicals

N, N-dimethylformamide (DMF), silver nitrate, concentrated ammonia, L-ascorbic acid and ethanol are purchased from Sinopharm Chemical Reagent Co., Ltd. Potassium citrate is purchased from Nippon Pure Chemical Co., Ltd. Thermoplastic polyurethanes (TPU) are bought from Ningbo Kingsui Rubber Plastic Co., Ltd. Boric acid and hydroxypropyl methyl cellulose (HPMC) are purchased in Aladdin Reagent Shanghai Co., Ltd.

4.2.2 Preparation of AgNF

Firstly, we stir 50 mL silver nitrate solution (0.3 M) and 50 mL potassium citrate solution (0.15 M) together at 50 °C for 2 min to obtain white silver citrate complex. After that, ammonia is added until the solution became clear, and then 50 mL of boric acid solution (0.5 M) is added to adjust

the pH value of the solution. Finally, 50 mL L-ascorbic acid solution (0.3 M) is added and reacted for 15 min. The solution immediately turns black indicating AgNF synthesis. AgNF is collected by vacuum filtration of a mixed fiber membrane with an aperture of 0.22 μ m and rinsed with a large amount of deionized water. After drying for 12 h at 40 °C in a vacuum drying oven, the mass of AgNF obtained is 1.6 g.

4.2.3 Preparation of AgNF layer

AgNF of different masses are dispersed in 20 mL ethanol by ultrasound to obtain different concentrations of AgNF dispersions. The AgNF dispersions are poured into a petri dish with a diameter of 90 mm and dried in an oven at 60 °C for 1 h to obtain AgNF layer.

4.2.4 Preparation of HPMC/AgNF film

At 70 °C, hydroxypropyl methyl cellulose (HPMC) of different masses are added to 10 mL deionized water and stirred to obtain HPMC solutions of different concentrations (0.001 g/mL, 0.003 g/mL, 0.006 g/mL, 0.012 g/mL). After cooling, 0.3 g AgNF is added and stirred for 12 h. After that, the mixture is dispersed by ultrasound for 30 min with probe ultrasound (power: 60%). Finally, the mixture is treated by vacuum drying oven for 1 h to remove bubbles in the solution. The mixture is poured into a petri dish with a diameter of 90 mm and dried in an oven at 60 °C to obtain HPMC/AgNF film.

4.2.5 Preparation of TPU/AgNF composite strain sensor

The specific process is to dissolve 1.5 g TPU particles in 8.5 g DMF, stir them at 60 °C for 6 h until a uniform TPU solution with a concentration of 15 wt% is obtained, and then cast the TPU solution on the AgNF film. The TPU/AgNF composite film is obtained after drying it in a blast drying oven at 60 °C for 10 h, and then the TPU/AgNF composite film is peeled off from the petri dish. Cut the TPU/AgNF composite film into a rectangular shape of 60×10 mm. In order to eliminate the contact resistance and better accept the resistance signal, the copper wires are glued to the both ends of the TPU/AgNF composite film with silver paste, and the strain sensor is obtained by curing at 60 °C for 2 h.

4.2.6 Preparation of M-CPC (TPU/HPMC/AgNF) strain sensor

Similarly, the preparation process of M-CPC strain sensor is the same as that of TPU/AgNF strain sensor. The uniform TPU solution with a concentration of 15 wt% is cast on the HPMC/AgNF film and dried in a blast drying oven at 60 °C for 10h to obtain the M-CPC film. We cut the M-CPC film peeled from the grinding tool to the appropriate size. Copper wires are glued to both ends of M-CPC film with silver paste and cured at 60 °C for 2 h.

4.2.7 Characterization

The polarizing microscope (Nikon ECLIPSE, LV100) and the field emission scanning electron microscopy (FESEM, Hitachi S-4800) are used to characterize the microstructure of samples and their composites. Energy dispersive X-ray (EDX) spectra are used to observe the element distribution in the cross section of brittle fracture samples. The crystal structure of AgNF is determined by an X-ray diffractometer (XRD, Bruker D8 Advance with Cu K α radiation λ =0.15406 nm). Fourier transform infrared (FT-IR) spectroscopy (Alpha, Bruker, Karlsruhe, Germany) verified the physico-chemical composition of the sample. Thermogravimetric analysis (TGA, Mettler Toledo) is used to determine the degree of thermal decomposition and component content in M-CPC. An Instron Mechanical Tester (model 3367) is used to determine the mechanical properties of the nanofiber composites under the test rate of 50 mm·min⁻¹. Surface resistance and resistivity of different samples are carried out by four-probe resistance tester (RST-9).

4.2.8 Strain sensing performance measurement

The strain sensitivity is the most important evaluation criterion of the strain sensor. To avoid possible errors under unstable conditions, M-CPC samples are pre-stretched 20 times before recording the sensor signal. The M-CPC samples are assembled into sensors using conductive silver paste and copper wire, and fixed with conductive adhesives. The M-CPC is connected to a resistance meter (DMM4040) for real-time monitoring of resistance changes during the stretch-release process. Transient resistance and initial resistance, represented by *R* and *R*₀ respectively, are important parameters of reaction sensing capability. ΔR represents the change of resistance, and the response value of the strain sensor is expressed by *R*/*R*₀. In general, the concept of strain sensor sensitivity is defined as the strain factor (GF), and its calculation formula is GF= $(\Delta R/R_0)/\Delta \varepsilon$, where $\Delta \varepsilon$ is the actual working strain.

4.2.9 Antibacterial test

In order to investigate the antibacterial properties of M-CPC, we use the method of constructing antibacterial ring on MH plate. Gram-negative *Escherichia coli* (ATCC 25922) and Gram-positive *Staphylococcus aureus* (ATCC 29213) are used as the experimental flora. First, the bacterial suspension is oscillated in an incubator at 37 °C for 12 h. Then, a double-layer agar medium is prepared, and 20 mL fused MH agar medium is spread on the bottom layer of a culture dish with a diameter of 90 mm. After cooling, a certain volume of bacterial suspension is added to the MH medium at about 37 °C to spread evenly. In the upper bacterial medium, the microbial density on 1 mL forming unit is about 10⁸-10⁹ colony-forming units (CFU). When the plate is hardened, circular thin films of TPU (control), TPU/AgNF and M-CPC are placed

on the surface (diameter is 6 mm; each group has three samples). After incubation at 37 °C for 24 h and 72 h, the antibacterial zones are observed.

4.2.10 Antibacterial activity evaluation

To demonstrate antibacterial effect more clearly, 4 mL LB broth is placed in glass test tubes and then autoclaved. The bacteria (*E. coli* and *S. aureus*) are inoculated to 1ml LB broth one night in advance, incubated at 37 °C for 12 h, and then added to the test tube to make the final CFU in the test tube reach 1×10^5 CFU/mL. Typically, TPU, TPU/AgNF and M-CPC specimens are immersed in bacterial suspensions for 24 h and 72 h. Set the culture medium without bacterial liquid and the bacterial liquid without any treatment as blank control and negative control, respectively. Each test is performed with three parallel samples. At each specific time, bacterial suspensions are subjected to turbidity analysis by a digital camera and the optical density is also detected at 600 nm by using a microplate reader. We calculate the bacterial inhibition rate according to the formula to provide specific results. Bacterial inhibition rate (%) = (B_{Control} - B_{Test})/B_{Control} × 100%

(where $B_{Control}$ and B_{Test} are the OD values of the negative control group and the test groups, respectively)

4.3 Results and discussion

4.3.1 Mechanism and composition

First of all, M-CPC is made of elastomer TPU as the flexible substrate, AgNF as the conductive nanofiller, and HPMC as the contact bridge to enhance bonding effect of the conductive nanofillers and flexible substrate, as shown in **Figure 4.1a**. According to the SEM and TEM images (**Figure 4.2a and b**), Ag cluster together to form the structure of AgNF. The crystal structure and diffraction pattern of AgNF are characterized by XRD in Figure 4.2c, which illustrates the characteristic peak position of Ag. The characteristic peaks are compatible with the diffraction angles and the intensities of the hexagonal structure of Ag JCPD card N. of 53-1847.³⁹ The AgNF have the potential as conductive nanofiller for CPC due to its large surface energy, surface activity, stability as a nanomaterial and excellent conductivity. HPMC, as an effective dispersant, can evenly distribute AgNF in its solution, so that the concentration of only 0.001 g/mL can present a uniform medium (Figure 4.3a). With the increase of HPMC concentration, HPMC/AgNF mixed solutions have different degrees of wall-retained phenomenon (Figure 4.3b and c). In addition, HPMC has excellent film-forming property, and Figure 4.4 shows the photographs of HPMC/AgNF films prepared with different concentrations of HPMC. Even at the concentration of 0.001 g/mL, AgNF can easily form a film in the Petri dish (Figure 4.4a), and it also can be seen that as the concentration of HPMC increases (Figure 4.4b-d), it leads to a smoother HPMC/AgNF film, due to the formation of the light HPMC film on the upper layer. Furthermore, Figure 4.5a illustrates the casting method to first prepare the AgNF embedded and dispersed by HPMC into a micron-scale film conductive network, and then cast TPU on the upper part of HPMC/AgNF to obtain the TPU/HPMC/AgNF (M-CPC). As a comparison, we also propose to the same casting method to directly modify the AgNF conductive film on the TPU substrate, and further analyze the related performance data. As shown in Figure 4.1, HPMC can be used to achieve the excellent dispersibility of AgNF and establish a strong contacting and bonding effect between the TPU substrate and the HPMC/AgNF conductive film through hydrogen bonds (Figure **4.1b**), at the same time indirectly improving the adhesive effect between

conductive AgNF and the TPU substrate. Visually, it is like a ship encountering wind and waves in the sea. When the anchor is dropped, the ship can stand stably on the sea, while the ship that has not anchored will drift with waves and even sink in the sea. Actually, ships are like AgNF, the sea is TPU that AgNF attempt to modify and provide with relevant properties, and the anchors are HPMC that can fix them with hydrogen bonds and interfacial interactions.



Figure 4.1 (a) Schematic comparisons of the TPU/AgNF and M-CPC strain sensor with the unique contacting structure. (b) Chemical structures of thermoplastic polyurethane (TPU) and hydroxypropyl methyl cellulose (HPMC). SEM images of TPU/HPMC-X/AgNF composite cross sections prepared by different concentrations of HPMC. X: (c) 0.001 g/mL, (d) 0.003 g/mL, (e) 0.006 g/mL and (f) 0.012 g/mL. SEM images of TPU/HPMC-X/AgNF composite surfaces prepared by different concentrations of HPMC. X: (g) 0.001 g/mL, (h) 0.003 g/mL, (i) 0.006 g/mL and (j) 0.012 g/mL.



Figure 4.2 (a) SEM and (b) TEM images of the AgNF, (c) XRD analysis of AgNF.



Figure 4.3 Different concentrations of HPMC-X/AgNF ink. X: (a) 0.001 g/mL, (b) 0.003 g/mL, (c) 0.006 g/mL and (d) 0.012 g/mL.



Figure 4.4 HPMC/AgNF film prepared with different concentrations of HPMC: (a) 0.001 g/mL, (b) 0.003 g/mL, (c) 0.006 g/mL and (d) 0.012 g/mL.



Figure 4.5 (a) Schematic diagram of the preparation process of TPU/AgNF and M-CPC strain sensors by casting. (b) Electrical conductivity, (c) Typical stress–strain curves and (d) Strain sensing performance ($\epsilon = 10\%$) of the M-CPCs with different concentrations of HPMC. (e) TGA and DTG curves, (f) FT-IR spectra and (g) XRD patterns of TPU and TPU/HPMC-0.001/AgNF (Final obtained M-CPC).

From Figure 4.1c-f, we can find that with the further increase of HPMC concentration, the contact part of HPMC/AgNF film and TPU substrate changes from the close fit at the beginning to different degrees of cracks. When the concentration of HPMC increases, AgNF agglomerations occur easily, which also induce the uneven distribution of HPMC at the upper and bottom part during the casting process of preparing HPMC/AgNF film, and the distribution amount of the bottom is significantly more than the upper (Figure 4.6). It means that hydrogen bondings between the TPU and HPMC/AgNF interfaces are negligible in the face of significant HPMC weight increase, resulting in some cracks occur between the layers. This phenomenon indirectly leads to a certain decrease in the number of hydrogen bonds that can be interacted with TPU at the upper part of HPMC/AgNF during surface modification, as the concentration of HPMC increases. For M-CPC, what we want is the HPMC/AgNF conductive network is not only the surface to conduct electricity, but as a whole to achieve the improvement of conductivity and build an impeccable conductive network. SEM image of M-CPCs surface shows superior dispersion and embedding effects of AgNF, with smooth surface and uniform particle distribution (Figure 4.1g). Figure **4.5b** illustrates the surface conductivity of M-CPCs measured by the four-probe resistance tester. Although the contents of AgNF are the same, the surface conductivity shows an upward trend as the concentration of HPMC increased. This phenomenon is attributed to a large amount of AgNF are deposited and agglomerated at the bottom (shift to the upper end and the surface part after M-CPCs are made) during the process of HPMC/AgNF film formation due to the increase of HPMC concentration (Figure 4.1h-j). Therefore, the surface conductivity shows a certain upward trend with the increase of HPMC concentration.

a	a-1	a-2	a-3	a-4
<u> </u>	b-1	b-2	b-3	b-4
c	c-1	c-2	c-3	c-4
d	d-1	d-2	d-3	d-4

Figure 4.6 Elemental mapping images of TPU/HPMC-X/AgNF, X represents the different concentration of HPMC. X: (a) 0.001 g·mL⁻¹, (b) 0.003 g·mL⁻¹, (c) 0.006 g·mL⁻¹ and (d) 0.012 g·mL⁻¹ (Elements: C, N, O, Ag).

As can be seen from Figure 4.5c, when the concentration of HPMC is 0.001 g/mL, the maximum elongation at break of M-CPC is 1082%. When the concentration of HPMC increases to 0.003 g/mL and 0.006 g/mL, the maximum elongation at break are 945% and 675%. In a certain range, the elongation at break decreases with the increase of HPMC concentration. In addition, when the concentration of HPMC is 0.012 g/mL, the elongation at break of M-CPC increases to 1072%. Because at high HPMC concentrations, the conductive HPMC/AgNF film has a poor combination with the TPU substrate. With the progress of several stretching-releasing cycles, the conductive layer would fall off from the substrate, resulting in the increase of elongation at break. Furthermore, Figure 4.5d illustrates the relationship between the HPMC concentrations of M-CPCs and the strain sensing performance. From the variation of signals, it can be found that the variation of response factor $(R_1: \text{maximum } R/R_0)$ is negatively correlated with HPMC concentrations, of which are 0.001 g/mL, 0.003 g/mL, 0.006 g/mL and 0.012 g/mL corresponding to 2.7, 2.8, 0.9 and 0.1, respectively. The R_I of M-CPCs with HPMC concentration of 0.006 g/mL and 0.012 g/mL is much lower than that of HPMC concentrations of 0.001 g/mL and 0.003 g/mL. Due to the fact that the HPMC/AgNF film of M-CPCs with the HPMC concentrations of 0.006 g/mL and 0.012 g/mL are not tightly bonded with the TPU substrate, which leads to the strain deformations mainly occur in the TPU substrate during the stretching and releasing process. High HPMC concentrations make HPMC/AgNF film exist a large number of AgNF agglomerations on the upper end and the surface, which are insensitive to small strains, resulting in no major damage to the conductive network, so the $R_{\rm I}$ is quite low. It is worth noting that the best HPMC concentration is 0.001 g/mL and the TPU/HPMC-0.001/AgNF is

the final obtained M-CPC.

Additionally, the TGA and DTG curves are used to clarify the weight loss of TPU and M-CPC during the thermal decomposition process (Figure 4.5e). The residual mass percentages of TPU and M-CPC after 800 °C are 4.8% and 16.4%, respectively.^{12, 23} Further, Figure 4.5f illustrates the FT-IR spectra of pure TPU and TPU/HPMC-0.001/AgNF. The peaks at 3332 cm⁻¹ and 1072 cm⁻¹ are the stretching vibration peaks of N-H and C-O-C in TPU.⁴⁰ And the absorption peaks at 1726 cm⁻¹ and 1529 cm⁻¹ are attributed to -NH-COOR ("amide I and amide II" bands in urethanes). After the HPMC/AgNF modification, the peak at 1726 cm⁻¹ shifts to 1689 cm⁻¹, indicating the interfacial interaction such as hydrogen bonding between TPU and HPMC.⁴¹ The absorption peaks of TPU are weakened due to the coverage of HPMC/AgNF film.⁴² As shown in Figure 4.5g, the crystal structures of TPU and M-CPC are analyzed by XRD. The pure TPU substrate has a broad diffraction peak from 15° to 30°, and the XRD pattern of M-CPC exhibits four sharp diffraction peaks at 38.3°, 44.5°, 64.7°, and 77.5°, corresponding to 111, 200, 220 and 311 crystal planes of AgNF.⁴³

4.3.2 Strain sensing performance

The purpose of this paper is to propose a new and subversive way to improve the physically selective surface modification of conductive nanofillers on the flexible polymer substrate. Therefore, in addition to the performance tests of M-CPC, we also perform the related strain sensing tests on TPU/AgNF, which do not conduct the HPMC modification. The preparation of TPU/AgNF strain sensor is similar with the preparation process of M-CPC (**Figure 4.5a**). AgNF is first dispersed with ethanol and made into a film, and then molten TPU is injected into the abrasive tool by casting, during which AgNF is adhered to the bottom

end of the TPU. The overall thickness of TPU/AgNF composite film is 108 µm, and the thickness of AgNF layer is 28 µm. Figure 4.7 shows the distribution diagram of C, N, O and Ag elements. C, N and O of TPU are also distributed in the AgNF layer, because the molten TPU will flow into the gaps between AgNF caused by the uneven dispersion. As shown in Figure 4.8, TPU/AgNF is further characterized by TGA, FT-IR and XRD. TGA and DTG results show that the residual mass percentage of TPU and TPU/AgNF after thermal degradation at 800 °C is about 4.8% and 40%. With the introduction of AgNF, the TGA curve of TPU/AgNF moves to the direction of high temperature. It can be seen from the stressstrain energy curve of Figure 4.8d that AgNF not only makes TPU film become conductive, but also increases the mechanical properties to a certain extent. However, the elongation at break of TPU/AgNF is reduced by 150% compared with TPU film, but TPU/AgNF still has a high elongation at break of 1100%, exhibiting great mechanical properties.



Figure 4.7 Elemental mapping images of TPU/AgNF.


Figure 4.8 (a) TGA and DTG curves, (b) FT-IR spectra, (c) XRD patterns and (d) Typical stress–strain curves of TPU and TPU/AgNF.

During the continuous strain sensing tests under small strains ($\epsilon = 0.5\%$, 1%, 3% and 5%), the $R_{\rm I}$ of TPU/AgNF shows an upward trend with the gradual increase of strain, which are 0.007, 0.009, 0.115 and 0.225, respectively (Figure 4.9a). It is worth noting that the initial resistance of TPU/AgNF also changes to varying degrees when the strain increases, which is a negative potential signal, indicating the instability and vulnerability of the outer AgNF conductive network. As shown in Figure 4.9b, when the strain sensing tests under large strains are carried out, the resistance change signals are relatively stable, and R_{I} increases with the gradual increase of strain. At the strain of 50%, R_I reaches 9.85. In addition, TPU/AgNF exhibits good signal transmission characteristics at large strain rates, but there exist some fluctuations at high strain rates (200 mm/min and 150 mm/min) (Figure 4.9c). Further, TPU/AgNF have five linear regions during the strain range of 0-50% and the GF has a certain increase from small strain to large strain, from 11 to 44 (Figure 4.9d). However, when TPU/AgNF is tested for 200 stretching and releasing cycles, the overall initial resistance and final resistance illustrate a quite obvious trend of growth, which indicates that the conductive network of AgNF loaded by physically selective surface modification method is quite unstable (Figure 4.9e). Such instability has been found at very low strain rates (20 mm/min), not to mention the performance at high strain rates.



Figure 4.9 The strain sensing performance of TPU/AgNF: (a) Resistance change under small strains ($\varepsilon = 0.5\%$, 1%, 3% and 5%) at a strain rate of 50 mm·min⁻¹; (b) Resistance change diagram under large strains ($\varepsilon = 10\%$, 30% and 50%) at a strain rate of 50 mm·min⁻¹; (c) Resistance change trends at different strain rates under the strain of 50%; (d) The entire linear fitting curves of TPU/AgNF; (e) Durability test of TPU/AgNF under repeated 20% strain for more than 200 stretching-releasing cycles at the strain rate of 20 mm·min⁻¹.

After the study and analysis of the composite without HPMC, the performance test of M-CPC is especially important. First of all, under the continuous small strain tests ($\varepsilon = 0.5\%$, 1%, 3% and 5%), the R_I of M-CPC shows a doubling increase trend, and it is gratifying that the initial resistance of M-CPC exhibits a very stable state without any change (Figure 4.10a). Additionally, when the strain gradually increases to 10%, 30% and 50%, R_I also significantly increases to 2.61, 3.28 and 7.52, respectively, and the initial resistance is still stable, as shown in Figure 4.10b. No matter at low or high stretch-release rates, the resistance change of M-CPC is stable, which further reveals the stability of the three-dimensional conductive network constructed by HPMC/AgNF thin film (Figure 4.10c). As can be seen from Figure 4.11, when M-CPC rapidly reaches 30% strain (strain rate: 1500 mm/min), the resistance response time of M-CPC is 125 ms and the resistance recovery time is 88 ms. Rapid response and recovery times endow the M-CPC with the ability to rapidly and continuously monitor subtle movements.



Figure 4.10 The strain sensing performance of M-CPC: (a) Resistance change under small strains ($\varepsilon = 0.5\%$, 1%, 3% and 5%) at a strain rate of 50 mm·min⁻¹; (b) Resistance change diagram under large strains ($\varepsilon = 10\%$, 30% and 50%) at a strain rate of 50 mm·min⁻¹; (c) Resistance change trends at different strain rates under the strain of 50%; (d) Strain sensing performance under $\varepsilon = 50\%$ at a strain rate of 50 mm·min⁻¹. (e) Durability test of M-CPC under repeated 15% strain for more than 500

stretching-releasing cycles at the strain rate of 20 mm·min⁻¹. (f) The initial linear fitting curve of M-CPC (0% < ε < 30%). (g) The entire linear fitting curves of M-CPC (30% < ε < 35%, 35% < ε < 40% and 40% < ε < 50%). (h) Comparison of strain sensing performance of various conductive polymer composites.^{13, 44-58} (i) SEM images of M-CPC at different strain during stretching and releasing to illustrate the strain sensing mechanism.



Figure 4.11 Instant response and recovery time of the M-CPC under a strain of 30% with the stretching rate of 1500 mm \cdot min⁻¹.

At the large strain of 50%, M-CPC also demonstrates excellent strain sensing performance, with $R_{\rm I}$ up to 1.75×10^6 (Figure 4.10d). Similarly, we test M-CPC for more than 500 stretching and releasing cycles at the strain of 15%. Surprisingly, the overall resistance and initial resistance of M-CPC have not changed at all during the whole process, with extremely superior stability (Figure 4.10e). Because HPMC can play a vital role to disperse AgNF as a whole, forming a three-dimensional HPMC/AgNF conductive network, and HPMC itself has good selfhealing property.^{37, 38} At a 3.0 mm/min stretch-release speed, the strength significantly dropped in the first 10 cycles, but remained almost constant in the last 290 cycles. Upon stretching-releasing cycles at a maximum strain of 50%, the M-CPC can retain more than 80% of its original maximum stress after the 300th cycles, as shown in Figure 4.12. Finally, Figure 4.10f shows that the GF of M-CPC is 27 when the strain is 2.5-30%. When the working strain gradually increases, GF achieves a great leap during the strain from 30% to 35%, reaching 2.8×10^7 . This is an ideal result, as few CPC strain sensors can achieve such a high GF at a small working strain, which can greatly improve the sensitivity and accuracy of M-CPC as a human motion monitoring sensor. According to the existing CPCs literature, the degree of skin surface deformation caused by limb movements is 15%-38%.^{2,3} As illustrated in Figure 4.10g, with the continuous increase of working strain, the GF of M-CPC decreases to a certain extent, which is 4.76×10^6 at 35%-40%. During the strain from 40% to 50%, the GF is 4.56×10^5 . Among the existing CPCs literature, the GF of M-CPC is relatively high, and it is the only one that can achieve extremely high GF under small working strains (Figure **4.10h**).^{13, 44-58} The further comparison details of the CPCs based strain sensors are summarized in Table 4.1.



Figure 4.12 Compressive stress–strain curve of 1st, 5th, 10th, 100th and 300th cycles.

Matrix	Conductive fillers	Working strain	Gauge factor	Author & Ref.
PVA	PA	100-140%	3.44	Shao et al. ¹³
Epoxy resin	CNTs	0.6-14%	6	Nag-chowdhury et al.44
PMVS	CNTAs/CB	0-60%	10	Ning et al. ⁴⁵
TPU	CB	0-20%	10.8	Zheng et al. ⁴⁶
PDMS	СВ	0-10%	15.75	Zheng et al. ⁴⁷
PVA	SA/TA	180-200%	15.98	Zhao et al. ⁴⁸
Aramid/PVA	Polyauiline	100-130%	39	Wang et al. ⁴⁹
TPU	Graphene pellets	50-100%	80	Choi et al. ⁵⁰
TPU	SWCNT/RGO	200-300%	114.7	Xu et al. ⁵¹

Table 4.1 Comparison of the strain sensing performance for conductive polymer composites extracted from literatures and our work.

PVA/golatin	CB	0-18%	523	Huang et al. ⁵²
TPU	MWCNT	5-50%	5200	He et al. ⁵³
PA6/PVA	CB	0-40%	9706.9	Zhan et al. ⁵⁴
OBC	CB	90-100%	1.40×10^{4}	Duan et al.55
TPU	CNT/AgNPs	200-250%	4.33×10 ⁴	Xiang et al. ⁵⁶
TPU	CNTs/GNP	150-250%	1.30×10 ⁵	Shajari et al. ⁵⁷
Fluoroelastomer	CNTs	85-100%	1.36×10 ⁵	Xiang et al.58
TPU	HPMC/AgNF	30-35%	2.8×10 ⁷	Our work

(CB: Carbon black; PA6: polyamide 6; PVA: poly (vinyl alcohol); TPU: thermoplastic polyurethane; CNTs: onedimensional carbon nanotubes; MWCNT: multi-walled carbon nanotube; PDMS: polydimethylsiloxane; SA: sodium alginate; TA: tannic acid; OBC: olefin block copolymer; PA: phytic acid; AgNPs: synthesized silver nanoparticles; PMVS: polymethylvinylsiloxane; SWCNT: single-walled carbon nanotube; RGO: reduced graphene oxide) Furthermore, we further observe the fractures of M-CPC with different strains from small to large under SEM (Figure 4.10i). At the original state, we can clearly observe that the surface of M-CPC is smooth. When the strain increases to 10%, the surface of M-CPC exhibits some obvious roughness compared with that of 0%. With the further increase of strain, M-CPC gradually forms regular fracture cracks along the direction of tensile mechanics when the strains are 30% and 50%, which cause great damages to the conductive network of HPMC/AgNF, and are also the key factor leading to the rapid rise of R_I when M-CPC experienced large strains. However, it is worth noting that during the whole stretching process, there is no phenomenon of AgNF shedding, which illustrates the stability of the three-dimensional conductive network constructed by HPMC/AgNF film, in which HPMC also serves as the supporting structure. Further, we gradually release the strain from 50% to 30%, and find that the originally large cracks have gradually healed and existed a tendency of complete healing. When the strain returns to 10%, the obvious cracks are almost all healed. Because the dispersant HPMC has a good self-healing property and can play a vital role in repairing the damage of HPMC/AgNF conductive network. Due to the stability and self-healing property of the HPMC/AgNF three-dimensional conductive network, M-CPC is endowed with excellent strain sensing performance, both for stability of stretching-releasing cycles and extremely high GF under small working strains.

4.3.3 Applications of M-CPCs

Because M-CPC has excellent strain sensing performance, especially high sensitivity under small working strain, it has great application prospect as a strain sensor in the field of human motion monitoring. As described in the relevant review paper, if the strain sensor can only produce high GF under large working strain, it is not of great practical value.⁵⁹ Actually, M-CPC can timely, clearly and stably reflect the changes of joint movements of human body through electrical signals (Figure 4.13a). First, M-CPC is used to detect different body movements of fist, elbow, finger, neck, wrist and knee, and the $R_{\rm I}$ detected are 2.51, 6.79, 7.12, 6.28, 10.62 and 11.34, respectively (Figure 4.13b-g). M-CPC shows excellent body motion monitoring ability, especially when compared with TPU/AgNF composite obtained by the selective surface modification method. In order to further highlight the advantages of M-CPC, we also set the TPU/AgNF strain sensor to detect different body movements of fist, elbow, finger, neck, wrist and knee. The corresponding $R_{\rm I}$ are 0.28, 0.35, 0.51, 0.34, 0.19 and 0.88, respectively (Figure 4.13b'-g'). Due to the irregularity and instability of its conductive network, TPU/AgNF composite only exhibits weak signal output and has certain signal fluctuations when it is used as a body motion sensor. As a comparison, M-CPC exhibits the much more clear and sensitive body motion monitoring performance than TPU/AgNF.



Figure 4.13 (a) Schematic diagram illustrating the M-CPC in monitoring mode for body motions. M-CPC (b-g) and TPU/AgNF (b'-g', as a comparison) serve as the wearable strain sensors for body motion monitoring: (b) fist, (c) elbow, (d) finger, (e) neck, (f) wrist and (g) knee.

Wearable strain sensors are mostly in direct contact with human skins, when worn for a long time, sweat and body fluids would overflow from the pores of the skin, which could easily cause bacteria to breed on the sensors, leading to the occurrence of some skin diseases. To overcome this obstacle, we set the antibacterial test for M-CPC, choosing two common trauma-causing bacteria as the experimental subjects: Gramnegative Eescherichia coli (E. coli, ATCC 25922) and Gram-positive Staphylococcus aureus (S. Aureus, ATCC 29213). TPU is used as the standard sample group for the experiments (Figure 4.14a and f), which do not have any antibacterial effect. However, TPU/AgNF shows good antibacterial properties (with obvious inhibition zones) on both E. coli and S. aureus agar medium plates, with diameters of 10.01±0.25 mm and 10.00±0.11, respectively (Figure 4.14b and g). When placed on the agar layer, AgNF would release Ag⁺, which can bind to the sulfhydryl groups (-SH) of the protein in bacteria and firmly adsorb, making them inactivated and coagulated. Further, the Ag⁺ can make some functional enzymes in bacteria lose their activities, which lead the internal mechanism of microorganisms disordered and eventually result in apoptosis. Furthermore, the antibacterial effect of TPU/AgNF only lasts for about one day. On the third day, it is found that the TPU/AgNF only exist very weak inhibition zone, because AgNF rapidly release Ag⁺ after being exposed to the bacterial environment (Figure 4.14c and h). It is worth noting that both TPU/AgNF and M-CPCs are endowed with outstanding antibacterial properties due to the existence of AgNF. M-CPC can exist two obvious inhibition zone on the two kinds of bacteria on the first day, with diameters of 10.23 ± 0.14 mm and 11.05 ± 0.17 , respectively (Figure 4.14d and i). However, due to the slow dissolution of HPMC in the bacterial growth environment, the HPMC dispersed and embedded AgNF can be released slowly along with the dissolution of HPMC, which has a relatively long-term antibacterial effect, comparing with TPU/AgNF. Even after 3 days, M-CPCs can still maintain their antibacterial effect on both E. coli and S. aureus with the inhibition zone diameters of 10.30±0.26 mm and 9.62±0.33 mm. Table 4.2 has summarized and compared the antibacterial effects of TPU, TPU/AgNF composite and M-CPCs under two different gram-bacterial environments. Furthermore, we analyzed the antibacterial activity of M-CPC by turbidity analysis, as shown in Figure 4.14k and I. For both TPU/AgNF and M-CPC, there was almost no turbidity in the suspensions after incubation for one day, indicating that bacterial reproductions of E. *coli* and *S. aureus* were significantly inhibited. However, the turbidity of TPU suspension was similar to that of the negative control. Interestingly, when incubated for three days, M-CPC suspension was still clear compared with turbidized TPU/AgNF suspension, indicating that M-CPC could effectively achieve sustained release of HPMC/AgNF, releasing a sustainable antibacterial effect. In the bacteriostatic rate test, there was a positive correlation between the bacteriostatic activity of CPCs and AgNF (Figure 4.14m and n). TPU/AgNF had higher antibacterial activity against E. coli and S. aureus at incubation time of 24h, with antibacterial rates of 70.45% and 64.04%. The bacteriostasis rates of M-CPC were 66.55% and 58.62%, respectively. However, TPU exhibited no obvious antibacterial activity, indicating that AgNF and HPMC/AgNF had antibacterial effects. After 72 hours of incubation, the bacteriostatic rate of TPU/AgNF decreased significantly, while M-CPC still maintained good bacteriostatic rate of 53.21% and 47.56% to E. coli and S. aureus. These results indicate that HPMC/AgNF developed in this research has significant and sustained antibacterial activity.



Figure 4.14 TPU, TPU/AgNF composite and M-CPCs (9 mm in diameter) are placed on agar plates cultured with common trauma bacteria, and the diameter of the zones of complete inhibition are measured. The experimental floras are: (a) TPU (Control, E. coli), (b) TPU/AgNF (E. coli, 1 day), (c) TPU/AgNF (E. coli, 3 days), (d) M-CPC (E. coli, 1 day), (e) M-CPC (E. coli, 3 days); (f) TPU (Control, S. aureus), (g) TPU/AgNF (S. aureus, 1 day), (h) TPU/AgNF (S. aureus, 3 days), (i) M-CPC (S. aureus, 1 day), (j) M-CPC (S. aureus, 3 days). Turbidity analysis of (k) E. coli and (l) S. aureus in liquid medium. Numbers 1-5 indicate TPU, TPU/AgNF (1 day), M-CPC (1 day), TPU/AgNF (3 days) and M-CPC (3 days), respectively. Comparisons of bacterial inhibition rate: (m) E. coli and (n) S. aureus. All data were obtained in three independent experiments and are shown as mean ±SD. n.s., not significant, *P<0.05, ***P*<0.01. ****P*<0.001. ****P<0.0001. determined by unpaired t-test.

Table 4.2 Comparison of antibacterial properties of TPU, TPU/AgNFcompositeandM-CPCsundertwodifferentgram-bacterialenvironments.

Samples	Inhibition Zone (mm)	Inhibition Zone (mm)	
	(E. coli, 25922)	(S. aureus, 29213)	
TPU	0	0	
TPU/AgNF (1 day)	10.01 ± 0.25	10.00 ± 0.11	
TPU/AgNF (3 days)	0	0	
M-CPC (1 day)	10.23 ± 0.14	11.05 ± 0.17	
M-CPC (3 days)	10.30±0.26	9.62±0.33	

4.4 Conclusion

The purpose of this paper is to propose a new way that can greatly improve the surface bonding effect of conductive nanofillers and flexible polymer substrates, thereby greatly enhancing the performance of CPCs as wearable strain sensors. In the preparation process, the most critical step is to use HPMC as the dispersant of AgNF and establish a strong interface interaction and bonding with TPU substrate, thus forming a three-dimensional conductive network of HPMC/AgNF film. The HPMC/AgNF conductive network endows the M-CPC with high conductivity, superior stretching-releasing stability, self-healing ability, great strain sensing performance and outstanding antibacterial property, which has outperformed traditional CPCs in many performance aspects. During more than 500 stretching-releasing cycles, M-CPC exhibits extremely stable resistance change signals that can be monitored cyclically. Additionally, M-CPC possesses an extremely high GF of 2.8×10^7 during the working strain from 30% to 35%, which is the highest GF of CPCs under small strains and has never been reported before. Both TPU/AgNF and M-CPCs are endowed with outstanding antibacterial properties on account of the existence of AgNF. However, due to the slow dissolution of HPMC in the bacterial growth environment, the HPMC dispersed and embedded AgNF can be released slowly along with the dissolution of HPMC, which has a relatively long-term antibacterial effect for 3 days, comparing with TPU/AgNF.

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Chapter 5. Conclusion

This thesis has given a comprehensive discussion on the fabrication methods, advanced mechanisms and strain sensing abilities of CPC strain sensors reported in recent years, especially the sensors with superior performance. To effectively avoid the increasing thresholds, decreasing conductivity, and improve the controllability and sensitivity of conductive networks of CPC strain sensors, I have pointed out the selective modification of conductive nanofillers on the surfaces of flexible polymer substrates, which contain the surfaces of polymer fibers and membranes.

In Chapter 1, the WCNC (TPU/ACNTs/AgNWs/PDMS) strain sensor consists of highly elastic TPU as the matrix, then the one-dimensional ACNTs network and the quasi-two-dimensional AgNWs layer network are assembled on the surfaces of TPU nanofibers and TPU/ACNTs nanofiber membrane in sequence. Finally, PDMS is introduced into WCNC, playing a role in protecting and fixing the AgNWs layer, and endows WCNC with great superhydrophobicity, self-cleaning ability and anti-corrosive resistance. Due to the synergy of the different dimensional conductive networks, the conductivity of WCNC is as high as 3506.8 S/m, leading WCNC to possess superior strain sensing performance. The GF of WCNC is as high as 1.36×10^5 , and it also exhibit a quite large working strain (from 38% to 100%). During the process of strain sensing, even cycled for more than 1200 times under the strain of 70%, WCNC still maintains good stability and durability. WCNC strain sensor can monitor a variety of human joint movements even under harsh environments, and realize the simultaneous and more precise body motion monitoring in multiple vertical directions.

In Chapter 2, the M-CNCs (TPU/ACNT/AgNF) strain sensor exhibits

unique dual shell structures, consisting of the basic elastic TPU substrate, the one-dimensional ACNT conductive network and the zerodimensional AgNF conductive network. TPU and its composite materials have great resilience and high elasticity after being stretched and compressed. The rigid ACNT and AgNF not only maintain the elongation at break of the composites almost unchanged, but also obviously improve the tensile strength of TPU/ACNT/AgNF at the strain of 0-400%. Additionally, the dual conductive networks endow the M-CNCs with great conductivity, strain sensing ability and antibacterial property. The conductivity of M-CNC (TPU/ACNT/AgNF) is up to 7.5×10^5 S/m. Further, the M-CNC strain sensor possess a large gauge factor of 55352 with the working strain ranging from 42% to 100%. The outer AgNF shell structure is stable even after the cyclic test for 1000 times under the strain of 50%. The AgNF also endow the M-CNCs with great antibacterial property, indicating brilliant growth inhibition effects on P. aureus and S. aureus.

In Chapter 3, a new way that can greatly improve the surface bonding effect of conductive nanofillers and flexible polymer substrates has been proposed, thereby greatly enhancing the performance of CPCs as wearable strain sensors. In the preparation process, the most critical step is to use HPMC as the dispersant of AgNF and establish a strong interface interaction and bonding with TPU substrate, thus forming a three-dimensional conductive network of HPMC/AgNF film. The HPMC/AgNF conductive network endows the M-CPC with high conductivity, superior stretching-releasing stability, self-healing ability, great strain sensing performance and outstanding antibacterial property, which has outperformed traditional CPCs in many performance aspects. During more than 500 stretching-releasing cycles, M-CPC exhibits

extremely stable resistance change signals that can be monitored cyclically. Additionally, M-CPC possesses an extremely high GF of 2.8×10^7 during the working strain from 30% to 35%, which is the highest GF of CPCs under small strains and has never been reported before. Both TPU/AgNF and M-CPCs are endowed with outstanding antibacterial properties on account of the existence of AgNF. However, due to the slow dissolution of HPMC in the bacterial growth environment, the HPMC dispersed and embedded AgNF can be released slowly along with the dissolution of HPMC, which has a relatively long-term antibacterial effect for 3 days, comparing with TPU/AgNF.

With the term of real applications, the continuous research and breakthroughs are essential to develop high performance CPC strain sensors for the advanced health monitoring system, which can improve the quality of our life.

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국문 초록

착용 가능하고 신축성 있는 스트레인 센서는 사람의 동작과 건강 모니터링, 유연 전자기기, 그리고 부드러운 로보틱 피부 분야에서 잠재력이 있다. 착용 가능하고 신축성 있는 스트레인 센서는 사람 피부에 직접 부착할 수 있고, 사람의 움직임과 개인 건강 관리를 위해 시각화된 관찰 정보를 제공한다. 전도성 필러와 유연 고분자로 이루어진 전도성 고분자 복합체 (CPC)는 고 신축성, 좋은 유연성, 우수한 내구성에 이점을 가지고 있으며, 넓은 작업 스트레인과 뛰어난 감도를 가진 유연한 스트레인 센서를 준비하는데 사용된다. 첫번째로, 유연하고 다기능성의 착용가능한 전도성 나노 섬유 복합체 (WCNC) 스트레인 센서의 손쉬운 제조 방법을 제안하였다. 산 개질된 탄소 나노튜브 (ACNTs)로 장식된 탄성 열가소성 폴리우레탄 (TPU), 연결하는 은 나노와이어 (AgNWs) 그리고 고체화된 폴리디메틸실록산 (PDMS) 로 구성되어있다. 순차적인 ACNTs, AgNWs 그리고 PDMS 장식은 TPU 기반의 나노 섬유질 막의 전도성, 초소수성 그리고 스트레인 감지 성능을 높인다. WCNC (TPU/ACNTs/AgNWs/PDMS)는 약 1.22 Ω/cm² (최대 전도도 3506.8 S/m) 로 꽤 낮은 저항, 우수한 초소수성(최대 접촉각 153.04°) 그리고 자정 능력을 가진다. 뿐만 아니라, WCNC 스트레인 센서는 고 민감도와 넓은 스트레인을 가지고 있는데 (38%에서 100% 로 작업 변형 시, 게이지율은 거의 1.36×10⁵), 이것은 WCNC 가 극도로 높은 게이지율에서 꽤 넓은 작업 스트레인을 가지고, 이는 이전에 보고된 적이 없는 것이다. 뛰어난 감지 성능으로 인해. WCNC 는 사람 몸의

여러가지 움직임을 모니터하는데 사용되어지고 동시에 다수의 수직 방향 센서 신호를 모니터하며,더 정확한 결과를 얻을 수 있다. 두번째로, 믿을만한 항균 능력을 가진 다기능 전도성 나노섬유 복합체(M-CNC) 스트레인 센서를 제시하였다. 열가소성 폴리우레탄 (TPU) 나노섬유는 기판으로 사용되고, 산 개질된 탄소 나노튜브 (ACNT) 로 꾸며진다. 원위치 자동 조립식 은 나노플라워(AgNF) 는 이중 전도성 네트워크를 가지며 M-CNC 로 불린다. M-CNC (TPU/ACNT/AgNF) 는 최대 7.5×10⁵ S/m 의 안정적인 전도성을 가진다.더 나아가, 이중 전도성 네트워크는 M-CNC 스트레인 센서의 감지 성능을 크게 향상시키고, 스트레인 42% 에서 100% 동안 55352 의 유용한 게이지율을 가진다. 추가적으로, 외부의 AgNF 껍질 구조는 스트레인 50% 하에서 1000 회의 사이클 후에도 안정적이다. AgNF 는 M-CNC 에 뛰어난 항균 성능을 부여하는데, 그람 음성 녹농균과 그람 양성 황색포도상구균에 눈부신 성장 억제 효과를 나타낸다.

세번째로, 유연성과 고전도성 그리고 항균 기능을 가지고 있고 하이드록시프로필 메틸셀룰로스 (HPMC)에 의해 내장된 열가소성 폴리우레탄(TPU)과 은 나노플라워 (AgNF) 로 구성된 다기능성 전도성 고분자 복합체 (M-CPC)를 제안하였다. 사실상, HPMC 는 AgNF 의 최고 분산성에 도달할 수 있고, 수소 결합을 통해 TPU 기판과 HPMC/AgNF 전도성 필름 사이에 강한 접착을 형성할 수 있다. M-CPC (TPU/HPMC/AgNF)는 높은 전도성과 사이클 안정성을 가진다. 더 나아가, HPMC 분산형 AgNF 전도성 네트워크는 M-CPC 에 우수한 스트레인 감지 성능을 부여하고, 극도로 높은 게이지율 (GF) 2.8×10⁷ (작업 스트레인: 30-35%) 을 지닌다. 이것은 작은 스트레인 하에서 CPCs 의 가장 높은 게이지율이며 지금까지 보고된 적이 없는 것이다. 게다가, HPMC/AgNF는 또한 M-CPC 의 항균성을 만드는데, 상대적으로 긴 3 일간의 항균 작용을 가진다. 실제 적용 기간과 함께, 지속적인 연구와 돌파구는 우리 삶의 질을 향상시킬 수 있는 선진의 건강 모니터링 시스템을 위한 고성능의 CPC 스트레인 센서를 개발하기 위하여 필수적이다.

주요어: 전도성 고분자 복합체, 웨어러블 스트레인 센서, 스트레인 감지 성능, 몸 움직임 모니터링

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