Surface strain regulation for stretchable electronics

Liu, Zhiyuan

2017

Li, Z. (2017). Surface strain regulation for stretchable electronics. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/72728>

<https://doi.org/10.32657/10356/72728>

NANYANG
TECHNOLOGICAL
UNIVERSITY

**SURFACE STRAIN REGULATION FOR STRETCHABLE
ELECTRONICS**

ZHIYUAN LIU

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2017

SURFACE STRAIN REGULATION FOR STRETCHABLE ELECTRONICS

ZHIYUAN LIU

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2017

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

.....
Date

.....
Zhiyuan Liu

Abstract

Stretchable electronics, such as stretchable electrodes and stretchable strain sensors, is vital for the soft electronics, such as human-like robots with artificial skins, wearable and implantable devices, and bionic sensory systems. However, how to achieve high stretchability, sensitivity, stability and adhesion by using simple fabrication procedures, is still a big challenge. In this thesis, a new strategy, surface strain regulation, is proposed to fabricate stretchable electrodes and strain sensors with high performance and accessible methods. The principle is that if the distribution of surface strain energy could be changed in the active material into a random style but not the concentration mode, it will turn into the network instead of throughout breaking at the strain concentration point. Based on it, more than five new material fabrication methods are developed: three of them for achieving stretchable active materials, and two for new sensors development and performance enhancement.

In detail, carbon nanotubes network by coffee ring effect, nanopiles interlocking, and dynamic interface mingling are the new methods proposed to achieve stretchable conductors. Hair-like and fiber-shaped structures are for new kinds of sensors and enhancing the performance. And they are all based on this new strategy/concept, surface strain regulation. The stretchable carbon nanotube thin film is successfully fabricated by coffee ring effect benefiting the high-gauge-factor stretchable strain sensors. For this stretchable conductor, the surface strain regulation is achieved by the carbon nanotube network structure. The film with gradient thickness successfully solved the problem of combining the contradictory properties of brittleness and stretchability achieving both high gauge factor and high stretchability. Also, inspired by the piling process in the building, a transitional layer from the soft substrate to the rigid active material is constructed to achieve the surface strain regulation by the new nanopiles interlocking structure. It is a new method to fabricate stretchable electrodes meanwhile addressing the solution for the adhesion problem between the active materials and substrate, which is the big obstacle for the real application of stretchable strain sensors. Moreover, a more accessible method by

dynamic interface mingling of elastic polymer and metal is reported here to fabricate stretchable conductors with high stretchability and stability, high surface area and most importantly, high adhesion between the metal, gold, and elastic polymer, PDMS in a large scale. The underlying knack is to use uncured PDMS instead of fully cured one to receive the gold atoms generated by the thermal evaporation. It will trigger a series of dynamic chemical and physical processes fabricating stretchable conductors with the unique microstructure of self-stripped kalst caves-like double layers. The self-stripped kalst caves-like layer can tune the strain distribution on top and achieve the superior performance. Further, a new kind of stretchable strain sensors, stretchable hair-like sensors with a design of gradient transition, has been proposed and produced by utilizing 3D printing and out-of-plane self-pinning effect, which will open up for exploration of stretchable hair-like sensors for soft electronic applications. By surface strain regulation of the hair-like structure, the sensitivity is enhanced and more importantly, the strain direction can be detected. Besides, a method to fabricate large-scale PDMS fibers is also proposed, by modifying the unique beads structure onto the fiber, the surface strain is redistributed and the sensitivity of the fiber-shaped stretchable strain sensors is significantly improved. All above news methods developed have proven the power of the new strategy proposed here, surface strain regulation for stretchable electronics. Based on it, many other methods could come up to fabricate new stretchable conductors and sensors.

Acknowledgements

I would like to give the sincere thanks to my supervisor, Prof. Chen Xiaodong, who is always inspiring, considerate and full of passion upon the research. He taught me a lot on the research skills. I will feel no surprise when I got his email sharing an exciting research news or an idea on the device fabrication/direction in the midnight. He also gave me full support on the research, organized fruitful discussion with other students and postdocs and constructed platform for us to communicate and cooperate with other domestic/international research groups.

I also sincerely thank my co-supervisor, Prof. Bo Liedberg, who is really kind, gentle and helpful, just like a grandpa. My Prof. always said to me that Prof. Bo is really nice and always willing to help young scientists and students.

I also would like to thank my uncle, a postdoc in our group, Qi Dianpeng who is always very helpful, generous and considerate. He taught me a lot on the research details and management, and always encouraged me when I felt depressed. He nearly knows every equipment in our lab and is willing to help everyone in our group.

I also want to thank other group members in my group: Zhu Bowen, Liu Yaqing, Yu Jiancan, Yang Hui, Li Bin, Xu Cai, Da Wang, Hu Guoyu, Jiang Ying, Chen Geng, Lu Ying; visiting professor Guo Peizhi, Qian Yan, Xu Huifang; cooperators: Prof. Shlomo Magdassi and Prof. Lorenzo Masia, and also technicians in MSE: Petrick, Zili, Wilson, Dr. Derrick.

Lastly, I am grateful for the full support from my family.

Table of Contents

Abstract	i
Acknowledgments	iii
Table of Contents	v
Table Captions	ix
Figure Captions.....	xi
Abbreviations	xxi
 Chapter 1 Introduction.....	 1
1.1 Hypothesis	2
1.2 Objectives and Scope	3
1.3 Dissertation Overview.....	4
1.4 Findings and Outcomes.....	7
References.....	7
 Chapter 2 Literature Review	 9
2.1 Methods to achieve stretchability.....	10
2.1.1 Current status of stretchable electrodes	10
2.1.2 Recent advancement of stretchable strain sensors	17
2.2 Defects sensitivity of the stretchable conductors	20
2.3 Adhesion of the stretchable conductors	21
2.4 PhD in context of literature	21

References	22
Chapter 3 Experimental Methodology	33
3.1 Polymer substrate and active materials preparation	34
3.2 Surface modification	39
3.3 Film deposition technologies	40
3.4 Synchronous testing of electrical and mechanical signals	43
3.5 Mechanical simulation	46
3.6 Image and data analysis.....	47
References	48
Chapter 4 Coffee ring effect of carbon nanotubes	49
4.1 Introduction	50
4.2 Experimental Methods	53
4.2.1 Carbon nanotubes solutions preparation	53
4.2.2 Coffee ring formation and characterizations.....	54
4.3 Principal Outcomes	57
4.3.1 Both high stretchability and sensitivity achieved	57
4.3.2 Isotropic stretchability	61
4.3.3 Long-term stability	64
4.4 Conclusions	65
References	66
Chapter 5 Hair-mimicking soft sensors by 3D coffee ring effect.....	71
5.1 Introduction	72

5.2	Experimental Methods	73
5.2.1	3D coffee effect of carbon nanotubes	73
5.2.2	Electrical and mechanical testing.....	74
5.3	Principal Outcomes	75
5.3.1	Stable hair-like sensor fabricated	75
5.3.2	Full stretchability of this sensor	81
5.3.3	Strain direction recognition.....	83
5.3.4	Air and water blow detection.....	90
5.4	Conclusions	92
	References	93
Chapter 6	Structured fibers for fiber-shaped stretchable strain sensors	95
6.1	Introduction	96
6.2	Experimental Methods	99
6.2.1	Transient curing of thermal setting polymer.....	99
6.2.2	Beads modification by Plateau-Rayleigh instability	101
6.2.3	Stretchable active materials deposition and performance testing	102
6.3	Principal Outcomes	102
6.3.1	Large-scale PDMS fiber fabrication	102
6.3.2	Beads modification on a single fiber	104
6.3.3	Sports motion monitoring	107
6.4	Conclusions	108
	References	110

Chapter 7	High-adhesion stretchable electrodes by nanopiles interlocking	115
7.1	Introduction	116
7.2	Experimental Methods	118
7.2.1	Nanopiles growth	118
7.2.2	Adhesion testing	120
7.2.3	EMG monitoring	120
7.3	Principal Outcomes	120
7.3.1	High-adhesion stretchable electrodes	120
7.3.2	EMG and mechanical strain monitoring	133
7.4	Conclusions	138
	References	139
Chapter 8	Synchronous interface forming of metal film and polymer for high-performance stretchable conductors	145
8.1	Introduction	146
8.2	Experimental Methods	147
8.2.1	Half-cured PDMS preparation	147
8.2.2	Thermal evaporation of gold film and other testing	147
8.3	Principal Outcomes	148
8.3.1	Large-scale high-performance stretchable electrodes	148
8.3.2	Principle of the stretchability achieved	153
8.3.3	Bio-electrical signal detection	160
8.4	Conclusions	162
	References	163

Chapter 9	Discussion and Future Work	167
9.1	General Discussion.....	168
9.2	Brittle layer to significantly enhance the sensitivity of stretchable strain sensors not included in main chapters.....	170
9.2.1	Brittle layer induced on PDMS.....	170
9.2.2	Sensitivity significantly enhanced	171
9.3	Encapsulation for stretchable electronics.....	174
9.3.1	Effect of the encapsulation to the performance	174
9.3.2	Preliminary results for the stretchable strain sensor	175
9.4	Future work: long-term implantation of the electrode and long-term stable stretchable strain sensors.....	177

Table Caption

Table 2.1 Comparison with other resistance-measurement based stretchable strain sensors.

Figure Captions

Figure 1.1 The surface strain regulation concept. If the strain is concentrated as shown in the left, the active material will break easily. But if the surface strain could be regulated to be a relatively randomly-distributed mode by certain structures design which will release the strain energy and achieve the conductive network.

Figure 2.1 Application background of the bio-electrical signal detection and present on-skin signals. All organs are connected with related neuros, so as long as these neuros can be connected and read out, the control of the organs is possible.

Figure 2.2 Scheme to show the overall principle to achieve stretchability. All the methods to achieve stretchability are based on this spring-like principle. The only difference is the component of the edge. Current reported methods includes from molecular-level design, nanowire-level one, to the macro structure design.

Figure 2.3 Current commercialized electrodes, including Utah, Caltech and Cuff electrodes to detect brain and peripheral neural signals.

Figure 2.4 Current progress of the stretchable electrodes for the bio-signal detection. Part of the published results are listed here, including the micro spring-based structure, micro gold film-based one and the ultra-flexible one.

Figure 2.5 Proposed methods to fabricate stretchable conductors. a) Composite of silver and multi-wall carbon nanotubes. b) Spring-like two-dimensional structures. c) Pre-stretching induced wrinkle structure. d) Stretchable mesh structures fabricated by controlled Grain-boundary of metal. e) Nanopiles interlocking as the transitional layer to increase the adhesion and achieve stretchability.

Figure 2.6 Young's modulus and the experienced maximum strain of related tissues and

the developed stretchable conductor.

Figure 2.7 Typical stretchable strain sensor reported recently. Gauge factor and stretchability are indicated in the green boxes

Figure 2.8 Typical fracture behavior of spring-like stretchable gold film. It would break at the strain concentration points located at the peaks and troughs

Figure 2.9 Poor adhesion of the normal stretchable gold film on PDMS substrate by controlling the gold film growth with initial nano-size defects.

Figure 3.1 The thickness-gradient film fabricated by using the self-pinning effect. a, The liquid level is pinned for the most of the evaporation time resulting in gradient structure. During the process, there would be the hydrogen bond between the carboxylic acid groups on carbon nanotubes and the hydroxyl groups on PDMS improving the adhesion. b, The original resistance of typical sensors with different plasma power for the hydrophilization treatment of PDMS substrate.

Figure 3.2 Flow diagram of e-hair fabrication. a, 3D printed mould with polylactic acid (PLA). b, PDMS film is coated on it. c, Cutting off with the stiffener stick inside. d, Partial hydrophilization with oxygen plasma. e, CNT solution is dropped on covering the whole root and part of the hair body under the help of capillary force. f, Out-of-plane multiple rings form on the hair body and root by 3D self-pinning effect.

Figure 3.3 Schematic diagram of the strategy of dynamic interface mingling and corresponding physical analyses. a) Diagram illustrating to show the fabrication process and uncured PDMS was used as the substrate to receive the evaporated gold. b) Physical models of heat transfer and viscous flow during the dynamic process. c) Simulation results

of the temperature distribution in the film and corresponding pressure distribution during the viscous flow under different viscosity (low viscosity in left and higher in right). d) Diagram of the unique self-stripping double-layer structure.

Figure 3.4 The coffee process after the CNT solution dropped to the surface after certain modifications.

Figure 3.5 3D coffee ring effect after proper surface modification onto the 3D structure.

Figure 3.6 Thin film with gradient thickness by coffee ring effect.

Figure 3.7 Multiple rings formation only by folding the substrate film. a, Diagram of the method of multi-ring formation. The PDMS substrate is folded, then made hydrophilic, and finally dropped with CNT solution in the corner. b, Image of fabricated multi-ring SWCNTs film. Red dash line illustrates the central line of the corner.

Figure 3.8 Three thin film growth modes for metal film by atoms stacking.

Figure 3.9 Diagram to illustrate the fabrication process of stretchable gold film with nanopiles. The green color shown for the Cu tape represents the adhesive material on the Cu film that is totally transferred to gold film after peeling off the sample from the Cu tape indicating the good adhesion of the sample.

Figure 3.10 Thickness-gradient stretchable gold film with initial nanocracks. a) The film was stretched by using a customized stretcher. b) Optical images of the film under different strain. c) The gauge factor enhancement by applying the proposed new strategy.

Figure 3.11 Dynamic stretching with resistance testing. The dynamic stretcher is at left side and the right shows the resistance testing equipment.

Figure 3.12 Image to show five-point encapsulation method (a) side view and (b) top view. Herein, liquid metal, with high mobility and surface tension which is ideal for flexible encapsulation, is employed to connect the sensing film with the bonding wires.

Figure 3.13 Air and water flow detection. a, Image to illustrate the detection of wide-range speed of nitrogen gas flow by tip-modified e-hair. b, Image to present the setup of detecting water flow. Diameter of the tube is 5 mm.

Figure 3.14 FEM simulation of the film with nanopiles underneath and without.

Figure 3.15 FEM simulation model and results. a) Model of the substrate with randomly oriented micro pillars. b) The strain regulation effect induced by the micro pillars.

Figure 4.1 The inspiration of gradient structure from Golden Gate Bridge. The force is transferred step by step from the most fragile part without supporting points to the main tower, by using the gradient suspended cable. Inspired by it, the thickness-gradient film for high-gauge-factor stretchable strain sensor is proposed.

Figure 4.2 Thickness-gradient films for obtaining high gauge factor and high stretchability. a,b) Demonstration images and FEM simulation showing the mechanism behind the property of stretchability of the rigid films on soft polymers, one piece of note paper on air in a), and strain energy is released by the wrinkles. Another one is fixed on a

substrate, there would be no wrinkles and the throughout crack appears when the tensile strain applied in b). Based on the principle of the stretchability, the 3D image in c) with the desired structure would possess both high stretchability and high gauge factor.

Figure 4.3 Self-spinning to fabricate thickness-gradient stretchable strain sensor. a) Fabrication process of the CNTs film by self-spinning effect. b) Tensile strain of 60% is applied by using a stretcher. c) The microscope image of the thick part. The thick, transitional and thin regions could be approximately located and divided by red dot lines, the surface morphology of which are presented in d), e) and f) respectively. And the wavelength of wrinkles is measured. It decreases from the thick to the thin region as shown in g), which illustrates the gradient thickness of the film according to buckling theory.

Figure 4.4 Surface morphology of the ring region under tensile strain of 5%. Low- a) and high- b) magnification of FESEM images of the thick ring part.

Figure 4.5 The 3D and 2D surface morphology of the thin region under 60% strain.

Figure 4.6 Coffee ring effect to fabricate SSSs with gradient thickness. a) Schematic of coffee ring process of SWCNTs film. b) The gradient thickness data of the film. c) One sample under stretch of the tensile strain of 60% by a customized stretcher. d) The optical image of the ring region in c). The wavelength of wrinkles differs from the thin to the thick region as shown in e). The thickness could be divided into four regions marked with four capitalized Roman numbers. SEM images to show the surface morphology of the thin, gradient and thick regions are presented in f), g) and h).

Figure 4.7 Stretchable strain sensor performance when applied with uniaxial strain. a) PDMS substrate tends to break, when the applied tensile strain is larger than 150%. b) The

stability of the sensor. The sensor keeps stable performance during the 100,000 strain cycles and the strain rate is 400 mm/min. Besides, it shows stable performance when 100% strain is applied in c). d) The gauge factors at different cycles. As presented in b), there are two linear regions when applied strain is less than 15% and larger than 25%. Two gauge factors can be calculated.

Figure 4.8 The control experiment to present the importance of the thick part for the gauge factor improvement. a) The amplified present of the resistance changing before 15% strain. b) The resistance changing under the cyclic strain of 100% (20,000 cycles). c) The detailed data after applying 60% uniaxial strain of 100,000 cycles. d) The resistance changing under different temperature at 100% uniaxial strain.

Figure 4.9 The control experiment to present the importance of the thick part for the gauge factor improvement.

Figure 4.10 The durability and the surface morphology under isotropic strain. According to the mechanical simulation in c), sensors are fabricated in the strain concentration area as shown in b) and the top view a). The resistance changing with the isotropic strain is shown in d). Utilizing the high stretchability, the LED circuit still works when suffering sharp bending, 1D stretching and isotropic strain as shown in e). The signal driven by the rhyme “little star” is presented in f). The numbered musical notation is listed on top and below every peak induced by the note. Insets present the amplified two same melodies.

Figure 4.11 The durability and the surface morphology under isotropic strain. a) The resistance changing under different cyclic isotropic strain. b) The FESEM image of the sensor under uniaxial strain of 60%. c, d) The Low- and high- magnification of FESEM images of the sensor under isotropic strain of around 85%.

Figure 4.13 The weak sound detection by using the novel sensor. a) The different pitches detected by the sensor. b) The displacement of the freestanding PDMS film under eigen vibrations. Accordingly, the sensor could be fabricated in the center covering certain area to detect different vibrations.

Figure 5.1. Demonstration of the real tactile hairs. a, Images to present the stretchability of the tactile hair. b, Extension-force curve of a real tactile hair on the forearm of an adult Asian man.

Figure 5.2 Bio-inspired stretchable tactile electronic hairs and structural mechanical optimization. a, Diagram of the response of tactile hairs to mechanical stimuli, and the stretchable tactile electronic hairs inspired by this process. b, Three-step mechanical optimization based on energy conservation and classical bending moment theory, and four structures (I, II, III, IV) developed correspondingly. The final optimized structure (IV) comprises two parts: a hair body with a stiffener of polylactic acid (PLA) and a hollow root. c, The strain concentration and distribution under the bending angle of 45° as calculated by FEM simulation for the four different structures proposed in (b). The negative value reflects compression. d, Strain concentration in the four different structures in (a) under different bending angles. e, Strain distribution areas in the four structures in (a) under the bending angle of 45° .

Figure 5.3 FEM simulation for strain distribution of different e-hair structures. a-c, the topview and sideview of the e-hair with full substrate, hollow substrate, and hollow substrate with stiffener inside the hair body, respectively.

Figure 5.4 On-hair multiple rings and the corresponding application to detect on-hair strain distribution. a, Image of typical on-hair five rings. b, Surface profile data of the five rings in (a). c, The velocity and displacement monitored by high-speed camera. d, This multiple rings can be employed to test the detailed deformation on the hair by careful encapsulation.

Figure 5.5 Soft tactile electronic hairs with out-of-plane multiple rings by the 3D self-pinning effect and their performance with respect to strain sensing. a, Diagram of the slip-and-stick self-pinning effect which is essential for the formation of the out-of-plane multiple rings and CNT thin film on the e-hairs. b, Image of a fabricated e-hair. Inset illustrates the five-point encapsulation method. c, Optical images of the e-hair during stretch and the corresponding strain distribution by FEM method shown in d. e, Resistance change with different strain concentration applied to the sensing unit. Normalized resistance, R/R_0 , where R and R_0 are the resistance values monitored with and without applied strain. The inset shows how the strain is applied. f, The durability of the e-hair under tensile strain. Tensile strain of 120% at the sensing unit was applied for over 10,000 strain cycles.

Figure 5.6 E-hair fabricated with diameter of around 25 μm . a, Image of the fine e-hair. b, FESEM image of the gradient root. c, Typical cracks and wrinkles structure on the root.

Figure 5.7 Comparison of relative resistance change between the structure with hollow root and the full root. Result shows that the resistance changes more significantly in hollow root than that in full root, indicating that the strain transferring is more efficient in hollow one

Figure 5.8 The resistance network modeling based on the strain distribution and related surface morphology under bending strain. a, Normalized resistance with different bending angle in different strain regions (see Supplementary Fig. 1a). b, The durability of the e-hair under bending strain. The inset presents the diagram of tensile strain and compression strain regions with black color and pink color respectively. c-d, Cracks and wrinkles distribution in tensile region (Region i) and compressed region (Region iii) under the bending angle of 60° , respectively. e, The resistance network is abstracted through three-step modeling. The four regions correspond to that analyzed in Supplementary Fig. 2 and the four resistors in the final model.

Figure 5.9 Isotropic stretchability of the e-hair array. Images to present how the

isotropic strain is applied in practice with smaller strain in (a) and larger strain in (b). c, The e-hair array could be used to identify the touching pattern, like a 'NTU' pattern.

Figure 5.10 Direction recognition when the direction of the bending strain slopes to that of encapsulation wires. a, Diagram to illustrate this situation under five-points encapsulation method. b-e, The resistance changing testing from point A to corresponding points, respectively.

Figure 5.11 FESEM images of the e-hair under bending strain. a, Image to present the boundary (red dash line) between the region iii and region iv as shown in Figure 3a. b, The on-hair multiple rings (between red dash lines) under the bending strain. The hair body is rotated to make it in horizontal under the FESEM. c, The lower ring on the root (between the red dash lines). Inset illustrates the typical magnified view of an area beside the lower ring on the root.

Figure 5.12 Results of resistance network modeling and related experimental data for reference. a, Resistance changing predicted by the resistance network model in Figure 3e. b, Experimental data of the resistance vibration from point B to point C.

Figure 5.13 Gradient wavelength from the thick on-hair ring part (region ①), transitional part (region ②) to inner thin part (region ③). a, On-hair thickness-gradient SWCNTs film. The e-hair is rotated to make the on-hair ring in horizontal under FESEM. The on-hair film can be roughly divided into three regions: thick ring part (①), transitional part (②) and inner thin part (③), according to the wavelength of the wrinkle corresponding to the thickness of the film. b, The detailed observation of the thick ring part in (a) and the definition of the wavelength. c, Wavelength changing in different regions.

Figure 5.14 Isotropic stretchability of the e-hair array and detection of subtle fluid flow. a, Photograph of the e-hair array. b, The normalized resistance change under different speeds ranging from 1 m/s ~ 11 m/s. c, The stability of the detection signals under the nitrogen speed of 5.7 m/s. d, The amplified view reveals that the damping vibration

dominates the later part of the signal as illustrated in the inset. e, Signal obtained under different water speeds corresponding to two different flow states: laminar flow and turbulence flow. The green square indicates a typical signal of laminar flow and the inset shows the magnified view. The red ellipse highlights the typical vibration signal of the e-hair driven by the turbulence flow. The red rectangle shows the signal induced by the sudden shut-off of the water flow.

Figure 5.15 Resistance response for different applied gas speed of nitrogen: 3.3 m/s in (a) and 1m/s in (b).

Figure 6.1 Proposed surface strain redistribution strategy to enhance the sensitivity of fiber-shaped sensors, and the fabrication process inspired by droplet splitting. a) FEM simulation to investigate the strain regulation effect of the micro-structured fiber as compared to the smooth fiber. b) Strain distribution along the fiber surface for the different structures in a). c) Inspired from the phenomenon of oil droplet splitting, the structured fiber in a) could be fabricated accordingly to regulate the strain distribution.

Figure 6.2 Tensile strain of the design structure simulated by using FEM method to indicate the strain redistribution effect by the larger volume. The modulus of the larger square region (blue region in the picture) is ten times larger than that of the fiber.

Figure 6.3 Illustration of the fabrication process of PDMS fibers with beads. a) PDMS fibers are fabricated sequently by viscosity control, dynamic traction and transient curing in silicon oil at 170-180 °C. b) After being cleaned and dried, beads are formed according to the principle of Plateau-Rayleigh instability, by controlling the Bond number. c) By keeping other fabrication parameters constant, the fiber diameter can be tuned by adjusting the dynamic viscosity. The inset formula represents the red fitting curve. d) Influence of the dynamic viscosity of the PDMS precursor on the bead diameter. The inset red curve shows the predicted value by the theory.

Figure 6.5 a) The viscosity changes with pre-curing time. b) Evolution of the fiber

profile with time under gravity (within 3 seconds). c) The related profile at 3.4 seconds. d) Locally magnified region in c) to indicate the nonuniformity of the diameter of the fiber.

Figure 6.6 a) The profile changing trajectory of the fiber under gravity with different time period. b) Experiment data of the fiber diameter uniformity. Inset illustrates the diameter measurement points on one fiber.

Figure 6.7 a,c) Fibers with diameter of around 90 μm and 10 μm under lower magnification, and higher magnification is shown in b,d) correspondingly. e) Meters of length of the as-prepared fiber.

Figure 6.8 Beads-on-fiber stretchable strain sensors. a) The stretchable gold film was deposited onto the structured fiber. b) Resistance changes as a function of applied tensile strain. c) Long-term stability of stretchable strain sensors upon exposure to 5000 tensile strain cycles at an applied strain of 30%. d) SEM images of the stretchable gold film at different locations along the fiber. e) Statistic analysis of the crack length in d). f) Quantitative analysis of the effect of the bead protrusion height on the strain sensitivity. Inset formulas represent the fitting curve.

Figure 6.9 a) Optical images of fibers with beads in different diameter, and the smaller one is observed in scanning electron microscope in b).

Figure 6.10 a) Resistance changes with different strain cycles for stretchable carbon nanotube film when tensile strain of 10% is applied to the beads-on-fiber sensors. b) Sensitivity comparison of fibers with and without beads.

Figure 6.11 Demonstration of the beads-on-fiber stretchable strain sensor for sports monitoring. a) Adhesion test of the PDMS film and the kinesiology tape. Reliable attachment was achieved by interlocking effect of the PDMS and the tape. b) The sensor with the tape was adhered onto the joint of lower limb to monitor the squatting. c) Detailed description of the wireless resistance monitoring chip. Also, the sensor can be used to

monitor the leg lifting. d,e) The typical raw data obtained by the fiber-shaped sensor when detecting squatting and leg lifting. The noise was induced by the limb natural vibration.

Figure 7.1 Proposed concept of nanopile interlocking to simultaneously achieve high adhesion and large stretchability. a) Diagram illustrating to show the principle of a tree standing firmly on the ground by stretching fractal roots into the soft soil. b) High-adhesion model. c) Inspired by it, just like piling process used in building, nanopiles are fabricated under the metal film to form the interlocking layer (equivalent to the transition layer in b)) between metal film and elastic polymer. d,e) FEM simulations of the strain distribution in the film with and without nanopiles under the tensile strain of 10%. f) Strain distribution along the dashed black lines in d, e).

Figure 7.2 Diagram to illustrate the fabrication process of stretchable gold film with nanopiles. The green color shown for the Cu tape represents the adhesive material on the Cu film that is totally transferred to gold film after peeling off the sample from the Cu tape indicating the good adhesion of the sample.

Figure 7.3 Adhesion enhancement and stretchability achieved by the nanopile and corresponding principles behind. a) Cross-section view of the fabricated stretchable gold film with nanopiles penetrating into the PDMS substrate. Insets show the front and reverse sides of the samples. The reverse is in black color induced by the absorption effect of the nanopile. b) Adhesion comparison of the nanopile film with normal crack-based stretchable gold film and flat non-stretchable film. c,d) Adhesion and stretchability performance with different film thickness for a given nanopile length of 1.5 μm , and different nanopile length for a given film thickness of 300 nm (inserts). e-i) FEM simulation to investigate the effect of film thickness and nanopile length on the strain distribution in the film under the tensile strain of 10%.

Figure 7.4 Images to show the fabricated samples. a, b) The effect of the adhesive material transferred from the copper tape to the gold film.

Figure 7.5 Images to contrastively illustrate the adhesion problem of the normal crack-

based stretchable gold film. a,b) The front and back side of the CSGF (left) and stretchable gold film with nanopiles (right). The back side shows typical yellow color for CSGF and black color for the nanopile film. c,d) The adhesion test by using Cu tape for film with nanopiles. Only a small amount of the film is removed by the tape. However, almost all gold film is removed for the CSGF sample showed in e,f).

Figure 7.6 Images to show the adhesion test process by using tensile in a) and tape method in for the sample with nanopiles in b-e) and the CSGF sample in f-i), respectively. The adhesive material on the scotch tape is even transferred to the gold film in d) indicating the excellent adhesion property for the sample with nanopiles. Nearly all gold film is removed by the tape for CSGF.

Figure 7.7 SEM images showing the fracture mechanism of the sample with nanopiles. It is clearly shown that part of PDMS is left among the nanopiles and that some of the piles are removed, indicating a good interlocking effect between the nanopiles and PDMS substrate. Additionally, the adhesion test was also conducted for stretchable CNT electrodes in c) and d).

Figure 7.8 The investigation of the effect of the porosity on the performance. a,b) SME images of two different AAO template with similar pore size but different porosity. c,d) Corresponding treatment by using open-code software Imagej to calculate the porosity. e) Stretchability and adhesion test with different porosity.

Figure 7.9 Images illustrating the unique feature of the crack-based principle to achieve stretchability. a) Front view of the NSGF and CSGF sample with the initial defect observed by optical microscope in b). c-e) The defect in the NSGF is the origin of the throughout cracks breaking the conductive path under strain. However, since the NSGF is based on the crack-based principle to achieve stretchability, the defect will not induce any strain concentration inside the film in f-h), although the defect already blocks more than half of the film, and the film still keeps conductive under strain.

Figure 7.10 SEM images illustrating the growth process of the gold film on AAO template. a-d) Different thickness of the gold film is deposited: 30, 50, 100, 300 nm respectively. Two typical features are observed: the grain size is relatively large (compare with Au film on glass, Figure S9c, d) and the morphology still reveals a porous state even for 300 nm thick films.

Figure 7.11 AFM images in amplitude mode (a-b) and phase mode (c-d) to clearly and quantitatively reflect the surface grain distribution. The grain size is as large as 200 nm and the porous-like state is evident.

Figure 7.12 SEM images of the gold film deposited on AAO template (a-b) and glass slide (c-d) under the same film growth condition showing the totally different grain size and morphology. The one on AAO is much larger than that on glass and most importantly, the porous state remains for that on AAO, but there is not for the flat gold film on glass.

Figure 7.13 SEM images to investigate the film transition before and after electrochemical deposition. a) a relatively thin film (80 nm) is deposited on AAO templated, and the porous state is kept. However, all pores are sealed after the electrochemical deposition and before forming the nanopiles underneath.

Figure 7.14 Mechanism of the stretchability and resistance change of the stretchable strain sensor. a-b) Surface morphology of the gold film with nanopiles under tensile strain of 0% and 30%, respectively. As comparison, the non-stretchable gold film under tensile strain of 30% is illustrated in c). d) The typical resistance change of stretchable gold film with nanopiles and non-stretchable gold film. It indicates the fracture of the film when the resistance is beyond the detection limit. e) Statistic analysis of the crack length in b, c). f) Resistance change under different applied tensile strain with more than 1000 cycles. The DC resistance changes in the small scale from around 5.5 Ω to 12.5 Ω which is only 1% of the interface impedance of the electrode, which has little effect on the EMG signal detection but can be utilized to detect strain.

Figure 7.15 a) Impedance of the electrode. At about 100 Hz, the impedance is around 1000 Ω which is much larger than the DC resistance of the electrode ($\sim 10 \Omega$). b) By using this electrode, the EMG signal can be detected and the amplitude spectrum analyzed.

Figure 7.16 High-adhesion stretchable silver electrodes based on this strategy. AAO template deposited with a) gold and b) silver. c) Following the similar fabrication procedure, stretchable silver electrode was fabricated.

Figure 7.17 Demonstration of the novel stretchable electrode and strain sensor detecting EMG signal and deformation induced by the elbow bending. a) Image illustrating the position of the fabricated stretchable electrodes and stretchable strain sensors and testing motion. b) Images of nanopile (left) and normal crack-based stretchable electrodes (right) after friction test. Red dashed boxes show the test region and the optical images present the corresponding magnified tested regions. c) EMG signal detected by the electrode with nanopiles after cyclic friction test. d) Energy spectrum analysis of the EMG signal showing the frequency range of main energy distribution. e) EMG signal detected by the CSGF after cyclic friction test. f) Signal-noise-ratio (SNR) comparison of those two electrodes.

Figure 7.18 The electrode can also be used as the stretchable strain sensor to detect the elbow bending in a), and the EMG signal by using the electrode before friction test is shown in b). c) EMG signal detected by commercial non-stretchable electrodes. d) Signal-to-noise ratio comparison between the nanopile stretchable electrode and the non-stretchable commercial electrode

Figure 7.19 A marker of red line on the biceps was used to demonstrate the strain in the skin for relaxing state in a) and contraction in b). The length change reflected the strain of the skin. c) The resistance change of the stretchable electrode during the motion.

Figure 7.20 The FEM simulation to calculate the strain transferred from the skin to the electrode.

Figure 7.21 The stretchable was sucked into the epoxy resin to become a non-stretchable electrode as the control. a) Image of the electrode. b) A typical EMG signal detected by this electrode. c) Amplitude spectrum analysis of the signal. d) SNR comparison of the free stretchable electrode and the fixed one

Figure 8.1 Schematic diagram of the strategy of dynamic interface mingling and corresponding physical analyses. a) Diagram illustrating to show the fabrication process and uncured PDMS was used as the substrate to receive the evaporated gold. b) Physical models of heat transfer and viscous flow during the dynamic process. c) Simulation results of the temperature distribution in the film and corresponding pressure distribution during the viscous flow under different viscosity (low viscosity in left and higher in right). d) Diagram of the unique self-stripping double-layer structure.

Figure 8.2 Structures of the film with and without strain applied. a,b) Cross-section SEM images of the self-stripping double-layer structure. Insets in a) show optical images of the front and reverse views of the sample with large area. The reverse is in black color resulted from the absorption effect by the gold nanoparticles and PDMS mingling layer. c,d) SEM and AFM images of the gold film showing the wrinkled structure with upheaval and depression. e) SEM image of the stretchable film under tensile strain of 50 %. Inset shows connecting bridge by the upheaval twisting. f) Resistance change under the tensile strain and it is out of the measurement range at around 135%. Inset presents the optical image of the testing process.

Figure 8.3 SEM images to further investigate the cross-section and surface structures. a,b) SEM images of the cross-section view. c,d) Detailed surface morphology of the conductor.

Figure 8.4 Different wrinkled structure with different ratio and pre-curing time. a-c) Different pre-curing time with the ratio of cross linker to monomer of 1:10. and for 1:20 in d-f).

Figure 8.5 Amplitude comparison of the wrinkle. a-c) AFM image and the section amplitude data shown in c). The film thickness is 300 nm (1:10, 25 mins). d,e) AFM image and the data for the same thickness film (1:20, 25mins). f) The amplitude comparison of the above two film.

Figure 8.6 Comparison of the wrinkles structures of our novel stretchable conductor and that fabricated by the traditional pre-biaxial strain method. a,b) Diagram to present the fabrication process of the pre-biaxial strain method. c) Typical wrinkled structure of the novel conductor for relatively thick gold film (200 nm). d) SEM image to present the surface morphology of the traditional film with the same film thickness.

Figure 8.7 Mechanism of the stretchability and the performance of the stretchable conductor. a-b) Finite element method simulation results to present the strain redistribution mechanism behind the stretchability. c) Resistance change under cyclic tensile strain. d) Stretchability vibration with different ratio of cross link to monomer and pre-curing time of PDMS. e) Stretchability and gauge factor affected by the gold film thickness. f) Adhesion with different ratio and pre-curing time.

Figure 8.8 SEM images of the stretchable conductor under tensile strain. a,b) The connecting effect by the twisting of the upheaval. c,d) The morphology of the film under 30% strain. The film is with cross linker to monomer ratio of 1:5 and pre-curing time of 25 mins, and the corresponding morphology for the film with 1:10 ratio and 25 mins pre-curing time is shown in e,f).

Figure 8.9 FEM simulation model and results. a) Model of the substrate with randomly oriented micro pillars. b) The strain regulation effect induced by the micro pillars.

Figure 8.10 Adhesion comparison by using Kapton tape. a-c) The testing process for the

flat non-stretchable gold film, and for normal crack-based stretchable gold film and the novel stretchable conductor in d-f) and g-i), respectively. j) The transient resistance measured by multi-meter to present the conductivity after the peel test in g-i).

Figure 8.11 Mingling effect of the evaporated gold and PDMS. a) SEM image to show the cross-section view of the gold film. b) The magnified view of mingling effect at the interface.

Figure 8.12 SEM images to show the fracture mechanism of the suspended film on PDMS substrate. a-b) Surface morphology of the bottom of the suspended film, indicating that the fracture point is near to the junction of the micro pillars and the film. c-d) The corresponding view of the morphology on PDMS substrate. Micro pillars are left on the substrate.

Figure 8.13 Demonstration of the novel stretchable conductor as the neural stimulator. a) Impedance of the electrode. Inset shows the fitting model to calculate the equivalent capacitance. b) Comparison of the equivalent capacitance of the wrinkled-surface novel conductor with the flat gold film. The capacitance is normalized by that of the flat gold film. c) Diagram of the set up to stimulate the sciatic nerve by the stretchable conductor and EMG monitoring system. d) Optical image to present the implanted stretchable conductor. e,f) Stimulation signal applied and the corresponding induced EMG signal detected.

Figure 8.14 Demonstration of the stretchable conductor as the neural stimulator. a) Setup of the stimulation and EMG monitoring. b) Peak-peak value of the induced EMG signal with different stimulation voltage.

Figure 9.1 Plasma Induced Brittle Layer Process.

Figure 9.2 a: The Illustration of Coffee Ring; b: The Illustration of a Sample Clipped in the MTS Strain Machine; c: The Illustration of a Sample with Brittle Layer at Small Strain; d: The Illustration of a Sample with Brittle Layer at Large Strain

Figure 9.3 a: The SEM Image of the CNT Part of a Sample with Brittle Layer; b: The SEM Image of the CNT part of a sample without Brittle Layer

Figure 9.4 a: The SEM Image of the CNT Part of a Sample with Brittle Layer with Mask; b: The SEM Image of the PDMS Part of a Sample with Brittle Layer with Mask; c: The SEM Image of the CNT Part of a Sample with Brittle Layer without Mask; d: The SEM Image of the PDMS Part of a Sample with Brittle Layer without Mask

Figure 9.5 Encapsulation process of the stretchable strain sensor.

Figure 9.6 a: The Relationship between resistance ratio and strain within 10% strain; b: The relationship between resistance ratio and strain within 30% Strain; c: The relationship between resistance ratio and strain within 60% strain.

Figure 9.7 a: Initial resistance-strain performance with undiluted encapsulation; b: Resistance-strain performance after one month with undiluted encapsulation.

Abbreviations

PDMS	Polydimethylsiloxane
SSSs	Stretchable Strain Sensors
SEM	Scanning Electron Microscopy
TFM	Transmission Electron Microscopy
GF	Gauge Factor

Chapter 1

Introduction

Stretchable devices are in fast development driven by the highly demands of more human-machine interfaces for applications in wearable electronics, healthcare, soft robotics, energy storage, and so on. These devices would change the healthcare style from the merely relying on hospital to the portable self-test mode, and also change the interaction manner of human with the robotics by assembling smart flexible sensors onto the robotics' skin. Besides, the soft battery package would also benefit the whole flexible electronics because it is critical for the power supply. Generally, the stretchable conductor is essential for connecting the working circuit of the flexible device, working as the current collector in the stretchable capacitors/batteries and directly monitoring physiological indicators. In detail, currently, various flexible sensors and capacitors, such as flexible tactile sensors, stretchable strain sensors, stretchable micro capacitors and batteries, have been fabricated and demonstrated. However, stretchable electrodes and strain sensors still undergo the exploring process because each application field proposes new requirements in terms of the integration of the electrode with other components. In this thesis, from the mechanics design, a new general strategy was proposed, surface strain regulation, to achieve a randomly-distributed fractures in the active materials releasing the strain energy and keeping the conductive network.

1.1 Hypothesis

Stretchable electronics, such as stretchable electrodes and stretchable strain sensors, is important for the soft electronics, such as human-like robots with artificial skins, wearable and implantable devices, and bionic sensory systems. However, the performances, such as stretchability, sensitivity, stability and adhesion, are still big challenges. This work on the stretchable electrodes and strain sensors will contribute to the exploration of stretchable interface with human beings, such as artificial exoskeletal system. Also, based on the new strategy and concept, many other material processes could be developed taking a solid step towards the real application of stretchable/soft electronics.

For a composite system of metal and polymer, the strain is normally transferred from the elastic polymer to the rigid metal, so this transferring process is critical to further achieve the stretchability of the metal, which means, the metal film or composite still keeps conductive under strain. Previously, people more focused on the design of metal or other active materials themselves, but this transferring process of strain was not fully utilized. In this thesis, the strain transferring is fully made use to fabricate stretchable conductors and high-performance sensors. The hypothesis is that, as illustrated in Figure 1.1, the surface strain regulation could be achieved by proper engineering of the strain transferring process. And then the distribution of strain energy in the active material could be changed into a random style instead of the concentrated one, lastly the active material will turn into the network structure instead of breaking at the strain concentration point. The big advantage of this strategy is that since the strain is released by numerous fractures, it will affect little on the stretchability if part of these fractures are removed which means that the stretchable active materials is damage/defects insensitive in the application.

Figure 1.1 The surface strain regulation concept. If the strain is concentrated as shown in the left, the active material will break easily. But if the surface strain could be regulated to be a relatively randomly-distributed mode by certain structures design which will release the strain energy and achieve the conductive network.

1.2 Objectives and Scope

The main objective of this thesis is to develop a new strategy and methods to fabricate stretchable electrodes and strain sensors with high performance, including high stretchability, long term stability, high adhesion between the active materials and the substrate, and high sensitivity for the strain sensor. Besides, in the real application, the damage to the active material is unavoidable, and to develop a defects/fractures insensitive stretchable materials is also the critical point.

In detail, the stretchable electrode is for the application of implantable neural interface or on-skin signal detection.^[1-5] For the implantable one, it would a long way to go to achieve a long-term stable electrode interface. There are many challenges, including the stretchability, softness, interface impedance management, adhesion, biocompatibility, encapsulation and so forth. The very first step is to achieve the soft stretchable electrode.

Stretchable strain sensors, as one of the critical components in wearable electronics, are under fast development driven by recent advances in integrating electronic components with humans to obtain the real-time mechanical feedback for applications in healthcare, rehabilitation, human power enhancement and so forth.^[6-11] But the sensitivity and stretchability are still to be investigated. Also, methods to enhance the sensitivity should

be also further studied and proposed.

The new strategy proposed here will give the community a new option to fabricate stretchable conductors with the unique properties of defects/fractures insensitivity, large stretchability, high adhesion and tunable sensitivity. Different methods developed based on this strategy already proved that the strategy is effective and furthermore, different other new methods could be proposed based on it.

1.3 Dissertation Overview

The thesis addresses how to achieve the stretchable electrodes and strain sensors based on the new proposed strategy: surface strain regulation to release the strain energy by numerous micro fractures keeping the conductive network at the same time. Different new methods are developed based on this new strategy which already prove the efficiency of this strategy.

Chapter 1 gives a rationale for this research. The hypothesis of controlling the surface strain distribution is proposed and analyzed, and the feature of this strategy is stated. The importance of achieving stretchable electrodes and strain sensors is elucidated.

Chapter 2 reviews the literature related to the methods to achieve stretchability and the state-of-the-art advancement of stretchable electrodes and strain sensors. The overall principle to achieve the stretchability is summarized and the feature and drawbacks of the present strategies are analyzed.

Chapter 3 discusses the methods which are employed to do the study including the polymer preparation, surface modification, thermal evaporation, electrical testing technologies, and so on.

Chapter 4 elaborates the first method developed based on this new strategy: surface strain regulation in the active materials. The carbon nanotube was employed as the active material and a very straightforward method, coffee ring effect, to fabricate stretchable carbon nanotube film with gradient thickness was developed. The detailed performance

data is presented and so are the principles. It is based on constructing the film with gradient thickness, which couples the seemingly contrary properties of brittleness and stretchability together to fabricate strain sensors with high gauge factor and large stretchability. The thickness-gradient film was formed by employing self-pinning effect of the single wall carbon nanotube solution. The fabricated sensor possesses surprisingly good performance covering all requirements of the sensitivity, stretchability and long-term stability. In this method, the surface strain regulation in the active materials is achieved by self-assembled carbon nanotube network structure itself. The randomly distributed defects form during the coffee ring process, after that, they grow into micro fractures when tensile strain applied.

Chapter 5 elaborates the stretchable hair-like sensors based on the three-dimensional coffee ring effect. In this work, the surface strain regulation is utilized to detect the strain applied direction. The fine hair on human body or animal skins is quite an excellent strain sensor. It can detect very tiny strain, e.g., the one induced by gentle wind. It would be important if this sensing function can be mimicked. The sensor fabrication and performance data is presented and discussed here. the 3D stretchable tactile electronic hairs (e-hairs) with isotropic stretchability, which can detect multiple strains and the strain direction (any direction) with high sensitivity and stability by each single e-hair, and the unique underlying detection principle relies on the symmetry breaking of the resistance network at the root. Besides, the fabrication process is all-solution based by employing 3D printing and a capillary force-assisted self-pinning of carbon nanotubes. The e-hairs can be easily fabricated in an array format for efficient monitoring of gas and liquid flow.

Chapter 6 elaborates the fiber-shaped stretchable strain sensors based on coffee ring effect of carbon nanotubes and micro-cracked stretchable gold film. In this work, by surface strain regulation, the strain concentration is induced at certain locations which enhances the sensitivity significantly. This work tends to shift the vision of improving the sensitivity of the stretchable strain sensor from the active materials engineering to the mechanical design of the elastic substrate. A novel strategy that enables surface strain redistribution in elastic substrate to significantly enhance the sensitivity is introduced.

Such enhancement method attributes to the delicate structure of beads on a fiber based on the principle of Plateau-Rayleigh instability. Also, a new method of transient thermal curing is proposed for large-scale fabrication of PDMS fibers with predefined diameter.

Chapter 7 introduces another new method to utilize the surface strain regulation achieving the stretchability, named nanopiles interlocking. In this work, the nanopiles interlocking layer serves as the transitional layer to tune the strain distribution mode in the active material to achieve the stretchability and high adhesion simultaneously. Inspired by a tree, a new method is proposed to fabricate high-adhesion stretchable electrodes that can be used as strain sensors with tunable stretchability, high gauge factor and stability. The nanopile not only provides the interlocking effect to significantly improve the adhesion, but also ensures that the tensile strain in the film is redistributed to release the strain energy by random cracks forming the connecting network and achieving the stretchability.

Chapter 8 elaborates a new method based on the strategy of surface strain regulation, dynamic interface mingling, to activate the synchronous forming of metal film and polymer at the interface. Dynamic interface mingling of elastic polymer and metal is utilized to fabricate stretchable conductors with high stretchability and stability, high surface area and most importantly, high adhesion between the metal, gold, and elastic polymer, Polydimethylsiloxane (PDMS). The underlying knack is to use uncured PDMS instead of fully cured one to receive the gold atoms generated by the thermal evaporation. It will trigger a series of dynamic chemical and physical processes fabricating stretchable conductors with the unique microstructure of self-stripped kalst caves-like double layers and the superior performance. The micro pillars in the cave will regulate the strain distribution in the active material to achieve the surface strain regulation achieving the stretchability.

Chapter 9 summarizes the whole thesis, and presents some preliminary results which are not shown in the main chapters and some challenges to be overcome.

1.4 Findings and Outcomes

This research led to several novel outcomes by:

1. Proposing a new strategy/concept, surface strain regulation, to fabricate stretchable electrodes and strain sensors. The performance of the electrode and strain sensors is significantly enhanced. Following this strategy, the community could propose more methods. Also, it is a new perspective for the stretchable electronics.
2. Developing more than five different methods based on the new strategy, respectively, to achieve the stretchability, fabricate high-adhesion stretchable electrodes, enhance the sensitivity of the stretchable strain sensors and demonstrate new mechanism to fabricate the sensors.
3. This new strategy and methods contribute to the community of stretchable electronics by providing the new perspective and opening up new paths.

References:

- [1] S. Choi, H. Lee, R. Ghaffari, T. Hyeon, D. H. Kim, *Adv. Mater.* **2016**, DOI: 10.1002/adma.201504150
- [2] J. Liang, L. Li, D. Chen, T. Hajagos, Z. Ren, S.-Y. Chou, W. Hu, Q. Pei, *Nat. Commun.* **2015**, 6, 7647
- [3] S.-K. Kang, R.KJ. Murphy, S.-W. Hwang, S.M. Lee, D.V. Harburg, N.A. Krueger, J. Shin, P. gamble, H. Cheng, S. Yu, Z. Liu, J.G. McCall, M. Stephens, H. Ying, J. Kim, G. Park, R.C. Webb, C.H. Lee, S. Chung, D.S. Wie, A.D. Gujar, B. Vemulapalli, A.H. Kim, K-M. Lee, J. Cheng, Y. Huang, P.V. Braun, W.Z. Ray and J.A. Rogers, *Nature*, **2016**, DOI:10.1038/nature16492.
- [4] B. C.-K. Tee and A. Chortos and A. Berndt, A. K. Nguyen, A. Tom, A. McGuire, Z. C. Lin, K. Tien, W.-G. Bae, H. Wang, P. Mei, H.-H. Chou, B. Cui, K. Deisseroth, T. N. Ng, Z. Bao, *Science*, **2015**, 350, 313.
- [5] J. Liu, T.-M. Fu, Z. Cheng, G. Hong, T. Zhou, L. Jin, M. Duvvuri, Z. Jiang, P. Kruskal, C. Xie, *Nature nanotech.* **2015**, 10, 629.
- [6] S. Lee, Y. Inoue, D. Kim, A. Reuveny, K. Kuribara, T. Yokota, J. Reeder, M. Sekino, T. Sekitani, Y. Abe, T. Someya, *Nature Commun.* **2014**, 5, 5898.

- [7] K. K. Kim, S. Hong, H. M. Cho, J. Lee, Y. D. Suh, J. Ham, S. H. Ko, *Nano Lett.* **2015**, 15, 5240.
- [8] M. Amjadi, K. U. Kyung, I. Park, M. Sitti, *Adv. Funct. Mater.* **2016**, 26, 1678.
- [9] J. Park, I. You, S. Shin, U. Jeong, *ChemPhysChem* **2015**, 16, 1155.
- [10] D. Qi, Z. Liu, W. R. Leow, X. Chen, *MRS Bulletin* **2017**, 42, 103.
- [11] X. Chen, *Small Methods* **2017**, 1, DOI: 10.1002/smtd.201600029.

Chapter 2

Literature Review

In this chapter, the state-of-the-art method to fabricate stretchable electrodes and strain sensors are reviewed. Related contribution and drawbacks of these methods are discussed. To achieve the stretchability is the very first issue for the stretchable electronics. People already focus on it for tens of years. Although the overall principle behind is just the mesh structure or “spring” structure, different materials and designs were proposed for different applications. But there are still some critical issues, such as adhesion between the active material and substrate, long-term stability, defects/damages sensitivity, and so on. In order to address them, the strategy of “surface strain regulation” is proposed.

2.1 Methods to achieve stretchability

Stretchable electronics is vital for the bio-integration of electronic components and biology,^[1-5] such as soft exoskeleton system,^[6] human-machine interfaces,^[7-9] and implantable bioelectronics.^[1, 10-12] As the core units, stretchable electrodes and strain sensors provide the basic platform for investigating the electrophysiology of tissues in vivo/vitro and mechanical deformation in medical therapy and tissue engineering.^[13-25] For example, integrated in the sensory skin, they can act as wearable assistive communication devices to track the illness and therapeutic effect (Figure 2.1).^[26-30]

- Signal decays by the tissue medium. E.g., 700 μV ECoG to 100 μV EEG.
- High frequency signal is filtered. E.g. 1000 Hz ECoG to 350 Hz EEG. *From Google Image*

Figure 2.1 Application background of the bio-electrical signal detection and present on-skin signals. All organs are connected with related neuros, so as long as these neuros can be connected and read out, the control of the organs is possible.

2.1.1 Current status of stretchable electrodes

Herein, stretchability is defined as that the electrode can still keep conductive under mechanical deformations and correspondingly, the critical strain, defined as the strain at which the electrode turns from being conductive to being non-conductive, is used to determine the stretchability.

Owing to their importance and that naturally there is nearly no intrinsic stretchable fully conducting materials, past decades have seen an extensive investigation upon how to make them with intrinsic rigid conducting materials and elastic polymers. Several strategies have been proposed including spring-inspired principle to which all in-plane/out-of-plane buckled methods and mesh construction are attributed,^[31-36] nanoparticle polymer composited,^[37-40] liquid assembled^[41-43] and crack-based method which can be used both for stretchable electrodes and strain sensors.^[44-49] To summarize them, the principle behind all the methods to achieve stretchability could be illustrated in Figure 2.2. The only difference is what has been chosen as the component of the edge of the mesh structure, and it could be as small as a molecular, nanowire and be as large as macro features, e.g., normal spring.

Figure 2.2 Scheme to show the overall principle to achieve stretchability. All the methods to achieve stretchability are based on this spring-like principle. The only difference is the component of the edge. Current reported methods includes from molecular-level design, nanowire-level one, to the macro structure design.

Stretchable devices are in fast development driven by the highly demands of more human-machine interfaces for applications in wearable electronics, healthcare, soft robotics, energy storage, and so on.^[50-57] These devices would change the healthcare style from the merely relying on hospital to the portable self-test mode, and also change the interaction manner of human with the robotics by assembling smart flexible sensors onto the robotics' skin. Besides, the soft battery package would also benefit the whole flexible electronics because it is critical for the power supply.^[58,59] In detail, currently, various flexible sensors and capacitors, such as flexible tactile sensors, stretchable strain

sensors, stretchable micro capacitors and batteries,^[60-63] have been fabricated and demonstrated. However, stretchable electrodes, the critical construction unit for flexible batteries and supercapacitors, flexible screen display, wearable sensors and implantable detectors, still undergo the exploring process because each application field proposes new requirements in terms of the integration of the electrode with other components. Generally, the stretchable electrode is essential for connecting the working circuit of the flexible device, working as the current collector in the stretchable capacitors/batteries and directly monitoring physiological indicators by replacing the rigid commercialized electrodes (Figure 2.3).^[64-73]

Figure 2.3 Current commercialized electrodes, including Utah, Caltech and Cuff electrodes to detect brain and peripheral neural signals.

Figure 2.4 Current progress of the stretchable electrodes for the bio-signal detection. Part of the published results are listed here, including the micro spring-based structure, micro gold film-based one and the ultra-flexible one.

Currently, many research groups focus on settling the stretchability (the critical strain of up to more than 300% has been achieved) by utilizing the composite of the elastic component: polymer (Polydimethylsiloxane (PDMS) is quite often used) and the conductive components: metal, carbon, and conductive polymer (Figure 2.4).^[74-78] Since the fully conductive materials is rigid, e.g., gold as the soft metal can only suffer no more than the tensile strain of 5%, so the spring-like structure plays the key role in achieving the stretchability. Normally, a spring is made of the rigid metal but possesses stretchability because of the geometrical construction. Most of the current approaches can be taken as the variants of spring-like structure no matter it is wrinkled, serpentine, cracked, or mesh structure. There is an intrinsic problem for wrinkled and serpentine structures. The stretchability achieved by using these methods is in the overall level, i.e., when you stretch the electrode at the very two ends, these two structures can be stretchable, however, if the tensile strain is locally applied along the conductive material wire at one basic unit of the spring-like structure, the conductor will suffer fractures immediately. So ideally, in order to keep stretchability, the conductor should have many sub-hierarchical units of the spring structure. The mesh and crack-based structures do not have the above disadvantages and are not sensitive to the strain concentration, because the deformation energy is already absorbed by the microcracks (Figure 2.5). This big advantage significantly benefits the stability of the electrode and also the surgery in practice because it is quite easy to induce defects/local damage during the practical operation. But the density of the crack and mesh should be carefully controlled, otherwise, if the typical scale of the crack and mesh is comparable with the width of the required electrode, e.g., 10 micrometers in width for monitoring one single neuro, the stretchability would be lost.

Figure 2.5 Proposed methods to fabricate stretchable conductors. a) Composite of silver and multi-wall carbon nanotubes. b) Spring-like two-dimensional structures. c) Pre-stretching induced wrinkle structure. d) Stretchable mesh structures fabricated by controlled Grain-boundary of metal. e) Nanopiles interlocking as the transitional layer to increase the adhesion and achieve stretchability.^[79-82]

But when the use of the stretchability is examined in detail, critical problems are be found which need to be clarified: why so large stretchability is required and how the soft electrode would be deformed when practically implanted *in vivo*, because it would be difficult to image that the beating heart will give the electrode a hand to stretch it just like during the electrode testing process and as described before, the body liquid may not give it a chance to provide enough friction force to make it stretched. However, the flexibility of the electrode, i.e., the bendability, requiring relatively small stretchability ($< 10\%$) is definitely needed, and in order to grantee the performance, large stretchability is required.

Moreover, softness is defined as the Young's modulus of the electrode including the apparent and the intrinsic, both of which are important for the mechanical matching between the electrode and the tissue for the medical use, because the tissue has the interaction with the attached electrode in both bulky and cell level. If the mechanical mismatching could not be overcome, there would be rejection reactions, tissue damages,

and even infection. Therefore, stretchability and softness belong to the different concepts and in theory should be satisfied at the same time.

It is noticed that although the softness of the electrode is important, it was not fully investigated compared to the stretchability. In order to propose solutions for this issue, how the implanted device interacts with tissues in the cell level should be studied, nevertheless, the detailed process of the cell response to the implanted electrode is still not clear until now. So at present, as the beginning step, the basic modulus matching should be achieved first.

Figure 2.6 Young's modulus and the experienced maximum strain of related tissues and the developed stretchable conductor.^[83-91]

Recently, for stretchable electrodes, PDMS is extensively employed as the soft substrate, while it possesses modulus of several MPa. Therefore, for the real application, the PDMS-based stretchable electrodes would be only applied to the tissue, e.g., dura, whose modulus is similar to PDMS, and would not adaptable to other soft organs, like brain, heart and so forth, which are also the critical application areas. Moreover, it should be noticed that even if the substrate is with the similar modulus with the target tissue, e.g., several hundreds/tens of kilo Pascals, the conducting material employed is still not as soft as the tissue! One way to solve this issue is supposed to modify it with soft hydrogel

maintaining the lower interfacial impedance. Electrode surface modification is quite important, and the related reviews could be referred^[84].

Futhermore, the stretchability and softness are required for the electrode to solve the issue of mechanical mismatching, however, they are not good for the doctors to operate the electrode in the practical surgery process, e.g., for the brain stimulation where electrodes are required to insert into the brain. Thus, how to achieve the switch of the softness and rigidity of the electrode is also important. Recently, dissolvable rigid back up and temperature-sensitive polymers were employed to assist to insert or operate the soft electrode. However it still requires to be further optimized in terms of the minimum damage to the tissue when inserting in and taking out, the fast-shifting and biocompatibility, and so forth.

Next, the adhesion issue will be discussed. Since as discussed previously, there is hardly fully conductive materials with high stretchability, as discussed previously, the composite of the polymer and metal were employed to fabricate the stretchable electrode. However, because the polymer had totally different physical properties and chemical properties with metal/carbon, there would be poor interfacial adhesion between them.^[92-96]

Normally, two methods were utilized to get the good adhesion: one was to construct chemical bonding between active materials and soft substrate; the other was to use the physical interlocking. Disulfide bond was extensively used to improve the interfacial adhesion between the gold film and the substrate. However, disulfide bond becomes not stable when the electrode is used for the implantable purpose. Therefore, physical method is still the good candidate. The transition layer could be constructed from the soft substrate to the active material. One of the methods was to build the interlocking layer, e.g., based on the nanopiles. The nanopile interlocking layer can help to achieve the large stretchability and the high adhesion at the same time. It should be noticed that good adhesion is vital for the stable performance and also quite important for the encapsulation, because the electrode not only needs to keep good adhesion with the substrate but also with the encapsulation layer normally also made of polymer. Therefore, it is important to construct double-interfacial layer for the good encapsulation.

For signal detecting, corresponding surface modifications to stretchable electrodes are

required to specifically monitor molecules or bio-electrical signals. Electrochemical reaction was utilized to detecting related biomarkers. Thus, the surface modification, by using paired molecules, aimed to enhance the chemical reaction at the interface. For bio-electrical signals, the electrode had to be modified, on the one hand, to make a soft interface with the soft tissue, and on the other hand, to lower the interface impedance to obtain high SNR signals. Platinum, conductive polymer (like PEDOT, PPy), hydrogel, and even the composite of gel and neural cells were used to decrease the impedance and enhance the long-term monitoring. However, it is still a big challenge to achieve the stable long-term monitoring. As mentioned, it is not clear upon how the tissue interacts with electrodes in the cell and gene level. Current modification still followed the original routine, like by using platinum, which had been already used since nineteenth century. And in 21st century, the biological study is booming and the corresponding knowledge will definitely benefit this surface modification.

2.1.2 Recent advancement of stretchable strain sensors

As one of the most interesting development approach to future electronics, the full fusion of human and electronic materials would be realized in the near future.^[97,98] More and more human friendly wearable and implantable electronics are being developed.^[99-105] Meanwhile, more human like robots with artificial skins^[106-109] and relevant sensory system are being created.^[110,111] All of those emerging devices demand one crucial component, stretchable strain sensors (SSSs), with large stretchability, high sensitivity and stability to monitor the strain state of the material itself or interfaces, which is crucial for the information feedback and system control.^[112,113] Those strain sensors can be extensively used in the therapy of movement disorders,^[114,115] micro strain detection in implantable medical devices such as artificial vessels implanted for aortic dissection therapy and neural interface electrodes,^[116,117] and heartbeat monitoring. They also play a key role in the construction of artificial sensory system for the robots, for which touch sensors, joint movement control and thermal expansion detection are all dependent on the SSSs.

Figure 2.7 Typical stretchable strain sensor reported recently. Gauge factor and stretchability are indicated in the green boxes.

The SSSs should have high sensitivity, uniaxial stretchability, durability and isotropic stretchability in order to provide effective and stable performance. On the one hand, since the strain suffered in vivo is relatively small for implanted strain sensors, it should have high sensitivity to recognize the signal, otherwise, no strain could be detected. On another hand, for the motion detection and joint monitoring, the high stretchability are required to match the large-scale stretch. Meanwhile, the durability and isotropic stretchability are also the necessary properties for the stable performance. Recently, many approaches have been proposed to fabricate the SSSs by employing carbon composites/nanotubes,^[118-123] metal/semiconductor hybrid structure,^[124-130] graphene-based materials,^[131-135] microfluidic devices,^[136] conductive polymer compositions,^[137-140] liquid metals and even 3D printing (Figure 2.7).^[141-144] However, it is still a big challenge to propose a principle to fabricate SSSs with all of those high performances, especially high gauge factor, stability, and uniaxial & isotropic stretchability, using an uncomplicated and facile method, which would be a solid step towards the novel and more practical stretchable strain sensor.

Table 2.1 Comparison with other resistance-measurement based stretchable strain sensors

Materials	Maximum Uniaxial strain	Maximum gauge factor	Durability (cycles)	Isotropic stretchability
CNTs*	150% (Decided by substrate)	160	100,000	Yes
CNTs ^[145]	180%	0.82	10,000	Not shown
CNTs ^[146]	150%	2.3	12,500	Not shown
CNTs & PEDOT ^[147]	100%	60	1000	Not shown
CNT fiber ^[148]	900%	64	10,000	Not shown
CNTs & Graphene ^[149]	100%	20,000	1000	Not shown
ZnO NWs ^[150]	50%	800	16	Not shown
Graphene ^[151]	8%	14	4	Not shown
Graphene ^[152]	150%	15	10	Not shown
Liquid metal ^[153]	100%	4.17	Not shown	Not shown
AgNWs ^[154]	60%	5.8	Not shown	Not shown
AgNWs ^[155]	80%	4.5	Not shown	Not shown
Pt-coated nanofibres ^[156]	4.5%	11.45	Not shown	Not shown
Carbon grease ^[157]	400%	3.8	1000	Not shown

* This work.

Except the normal flexible strain sensor, skin has been taken as the largest organ in human body, and even “brain on the outside”.^[158,159] As a most interactive part with the external mechanical stimuli, it possesses diverse tactile sensor components,^[160-163] and could be taken as a highly integrated, fast-response and highly sensitive soft strain-sensing device. Inspired by this, the booming interactive soft electronics also desire those strain-sensing performances, especially for memory devices,^[164,165] electronic skin^[166-168] smart robots,^[169,170] and other human-machine interface equipments.^[171]

Among all of those sensor systems in skin, one subcomponent plays a key role in the detection of subtle strain induced by air flow, insect climbing, and even sound resonance, however, easily tends to be disregarded since it is usually taken as a small affixture on skin. It is the hair, especially the sweat hair covered on most area of the body. When

you bend or blow your sweat hair, for example, on the forearm, the tactile signal will immediately be transferred to the brain. The hair can significantly enhance the tactile sensitivity, particularly for air/water flow and slight touch without touching on the skin directly. Besides, the hair on animals and plants are also of importance and even more powerful than that on human. Bats possess fine hair overlaid on the wing which has been proved to assist its flying sensing the airflow. Zebrafish equips with kinociliums in the center of neuromast on the lateral line to sense the water flow. The tiny trigger hair ambushed in the carnivorous plant Venus flytrap is sensitive to any kinds of touching which will begin a cascade of rapid actions to trap the insect. Therefore, if this highly sensitive detection mode could be mimicked, the performance of this sensor would be largely improved.

2.2 Defects sensitivity of the stretchable conductors

To achieve the stretchability is the very first step for stretchable electronics, however, the stability is also crucial for the application, which highly depends on the sensitivity of the electrode to the defects induced either by the initial fabrication or by the cyclic strain applied. The property of defects insensitive is quite important in the real application. Firstly, during the surgery, doctors will bring some damages unavoidably by sutures or by cutting to fit the tissue condition. In this situation, if the electrode is sensitive to those defects, the electrode would lose functions easily during the strain applied. Take the “spring-like” structure for example, it was already reported that the peaks and valleys in the structure were quite easy to break (Figure 2.8). So a new method has to be developed to fabricate stretchable electrode which should possess the defect-insensitive property.

Figure 2.8 Typical fracture behavior of spring-like stretchable gold film. It would break at the strain concentration points located at the peaks and troughs.^[172]

2.3 Adhesion of the stretchable conductors

Herein, adhesion refers to that between the active material, e.g., gold and the polymer substrate, e.g., PDMS. If with poor adhesion, the electrode will not be stable during the real application either for the *in-vitro* or *in-vivo* applications. Unfortunately, because there are totally different physical and chemical properties between inorganic materials which normally is the active materials, and the organic materials which is the soft substrate or holder, so bad adhesion is the common issue for the thin film electrode (Figure 2.9). It would be also correct for the composite structure, e.g., metal nanowires dispersed in the gel/polymer. In this case, there is still adhesion problem in the micro scale. It should be aware that the stable performance could not achieved without good adhesion. Adhesion is also critical for the encapsulation, because the electrode not only needs to keep good adhesion with the substrate but also with the encapsulation layer normally also made of polymer. Therefore, it is the critical issue to fabricate the soft stretchable electrodes with high adhesion.

Figure 2.9 Poor adhesion of the normal stretchable gold film on PDMS substrate by controlling the gold film growth with initial nano-size defects.

2.4 Ph.D. in Context of Literature

This work is to develop a new strategy to fabricate stretchable electrodes and strain sensors with high performance including high stretchability, sensitivity, stability and large-scale fabrication. The strategy should also solve the problem of defects insensitive and bad adhesion. The proposed new strategy is based on the concept of surface strain regulation, to fabricate stretchable electrodes and strain sensors. The principle is that if the distribution of surface strain energy in the active material could be changed into a random style but not the concentration mode, it will turn into the network instead of breaking at the strain concentration point. This will also solve the problem of defects insensitive because the strain energy is absorbed in a distributed manner and losing part of the film will not affect the overall performance. Also, the interfacial layer should be well engineered which will benefit the adhesion. Based on it, more than five new material fabrication methods were developed: three of them for achieving stretchable active materials, and two for new sensors development and related performance enhancement

References:

- [1] S. Choi, H. Lee, R. Ghaffari, T. Hyeon, D. H. Kim, *Adv. Mater.* 2016. DOI: 10.1002/adma.201504150
- [2] J. Liang, L. Li, D. Chen, T. Hajagos, Z. Ren, S.-Y. Chou, W. Hu, Q. Pei, *Nat. Commun.* 2015, 6, 7647
- [3] S.-K. Kang, R.K.J. Murphy, S.-W. Hwang, S.M. Lee, D.V. Harburg, N.A. Krueger, J. Shin, P. gamble, H. Cheng, S. Yu, Z. Liu, J.G. McCall, M. Stephens, H. Ying, J. Kim, G. Park, R.C. Webb, C.H. Lee, S. Chung, D.S. Wie, A.D. Gujar, B. Vemulapalli, A.H. Kim, K-M. Lee, J. Cheng, Y. Huang, P.V. Braun, W.Z. Ray and J.A. Rogers, *Nature*, 2016, DOI:10.1038/nature16492
- [4] B. C.-K. Tee and A. Chortos and A. Berndt, A. K. Nguyen, A. Tom, A. McGuire, Z. C. Lin, K. Tien, W.-G. Bae, H. Wang, P. Mei, H.-H. Chou, B. Cui, K. Deisseroth, T. N. Ng, Z. Bao, *Science*, 2015, 350, 313.
- [5] J. Liu, T.-M. Fu, Z. Cheng, G. Hong, T. Zhou, L. Jin, M. Duvvuri, Z. Jiang, P. Kruskal, C. Xie, *Nature nanotech.* 2015, 10, 629.
- [6] Y. Ding, I. Galiana, A. Asbeck, S. De Rossi, J. Bae, T. Santos, V. Araujo, S. Lee, K. Holt, C. Walsh, *IEEE Trans. Neural. Syst. Rehabil. Eng.* 2016, DOI: 10.1109/TNSRE.2016.2523250
- [7] S. Lim, D. Son, J. Kim, Y. B. Lee, J. K. Song, S. Choi, D. J. Lee, J. H. Kim, M. Lee, T. Hyeon, D. H. Kim, *Adv. Funct. Mater.* 2015, 25, 375.
- [8] S. Jung, J. H. Kim, J. Kim, S. Choi, J. Lee, I. Park, T. Hyeon, D. H. Kim, *Adv. Mater.* 2014, 26, 4825.
- [9] J. W. Jeong, W. H. Yeo, A. Akhtar, J. J. Norton, Y. J. Kwack, S. Li, S. Y. Jung, Y. Su, W. Lee, J. Xia, H. Cheng, Y. Huang, W.-S. Choi, T. Bretl and J.A. Rogers, *Adv. Mater.* 2013, 25, 6839.
- [10] D.-H. Kim, R. Ghaffari, N. Lu, J. A. Rogers, *Annu. Rev. Biomed. Eng.* 2012, 14, 113.
- [11] I. R. Mineev, P. Musienko, A. Hirsch, Q. Barraud, N. Wenger, E. M. Moraud, J. Gandar, M. Capogrosso, T. Milekovic, L. Asboth, R. F. Torres, N. Vachicouras, Q. Liu, N. Pavlova, S. Duis, A. Larmagnac, J. Vörös, S. Micera, Z. Suo, G. Courtine, S. P. Lacour, *Science* 2015, 347, 159.

- [12] S. P. Lee, L. E. Klinker, L. Ptaszek, J. Work, C. Liu, F. Quivara, C. Webb, C. Dagdeviren, J. A. Wright, J. N. Ruskin, M. Slepian, Y. Huang, M. Mansour, J. A. Rogers, R. Ghaffari, *Proc. IEEE* 2015, 103, 682.
- [13] D. Qi, Z. Liu, M. Yu, Y. Liu, Y. Tang, J. Lv, Y. Li, J. Wei, B. Liedberg, Z. Yu, X. Chen, *Adv. Mater.* 2015, 27, 3145.
- [14] T. Cheng, Y. Zhang, W. Y. Lai, W. Huang, *Adv. Mater.* 2015, 27, 3349.
- [15] C. Guo, Y. Chen, L. Tang, F. Wang, Z. Ren, *Nano Lett.* 2016, 16, 594.
- [16] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J.-H. Ahn, P. Kim, J.-Y. Choi, B. H. Hong, *Nature* 2009, 457, 706.
- [17] M.-S. Lee, K. Lee, S.-Y. Kim, H. Lee, J. Park, K.-H. Choi, H.-K. Kim, D.-G. Kim, D.-Y. Lee, S. Nam, J. U. Park, *Nano Lett.* 2013, 13, 2814.
- [18] C. Keplinger, J.-Y. Sun, C. C. Foo, P. Rothemund, G. M. Whitesides, Z. Suo, *Science* 2013, 341, 984.
- [19] T. Yamada, Y. Hayamizu, Y. Yamamoto, Y. Yomogida, A. Izadi-Najafabadi, D. N. Futaba, K. Hata, *Nature nanotech.* 2011, 6, 296.
- [20] X. Li, R. Zhang, W. Yu, K. Wang, J. Wei, D. Wu, A. Cao, Z. Li, Y. Cheng, Q. Zheng, *Sci. Rep.* 2012, 2.
- [21] J. T. Muth, D. M. Vogt, R. L. Truby, Y. Mengüç, D. B. Kolesky, R. J. Wood, J. A. Lewis, *Adv. Mater.* 2014, 26, 6307.
- [22] B. Sun, Y.-Z. Long, S.-L. Liu, Y.-Y. Huang, J. Ma, H.-D. Zhang, G. Shen, S. Xu, *Nanoscale* 2013, 5, 7041.
- [23] X. Xiao, L. Yuan, J. Zhong, T. Ding, Y. Liu, Z. Cai, Y. Rong, H. Han, J. Zhou, Z. L. Wang, *Adv. Mater.* 2011, 23, 5440.
- [24] C. Yan, J. Wang, W. Kang, M. Cui, X. Wang, C. Y. Foo, K. J. Chee, P. S. Lee, *Adv. Mater.* 2014, 26, 2022.
- [25] X. Wang, Y. Gu, Z. Xiong, Z. Cui, T. Zhang, *Adv. Mater.* 2014, 26, 1336.
- [26] K.-I. Jang, S. Y. Han, S. Xu, K. E. Mathewson, Y. Zhang, J.-W. Jeong, G.-T. Kim, R. C. Webb, J. W. Lee, T. J. Dawidczyk, R.H. Kim, Y.M. Song, W.-H. Yeo, S. Kim, H.Y. Cheng, S.I. Rhee, J.H. Chung, B.G. Kim, H.U. Chung, D.J. Lee, Y.Y. Yang, M.G. Cho, J.G. Gaspar, R. Carbonari, M. Fabiani, G. Gratton, Y.G. Huang and J.A. Rogers, *Nature Commun.* 2014, 5, 4779.
- [27] J. J. Park, W. J. Hyun, S. C. Mun, Y. T. Park, O. O. Park, *ACS Appl. Mater. Interfaces*

2015, 7, 6317.

- [28] X. Zhao, Q. Hua, R. Yu, Y. Zhang, C. Pan, *Adv. Electron. Mater.* 2015, 1500142.
- [29] M. Kubo, X. Li, C. Kim, M. Hashimoto, B. J. Wiley, D. Ham, G. M. Whitesides, *Adv. Mater.* 2010, 22, 2749.
- [30] L. Song, A. C. Myers, J. J. Adams, Y. Zhu, *ACS Appl. Mater. Interfaces* 2014, 6, 4248.
- [31] D. S. Gray, J. Tien, C. S. Chen, *Adv. Mater.* **2004**, 16, 393.
- [32] S. Xu, Y. Zhang, J. Cho, J. Lee, X. Huang, L. Jia, J. A. Fan, Y. Su, J. Su, H. Zhang, *Nature Commun.* **2013**, 4, 1543.
- [33] C. F. Guo, T. Sun, Q. Liu, Z. Suo, Z. Ren, *Nature Commun.* **2014**, 5, 3121.
- [34] J. Mertens, R. W. Bowman, J. C. Willis, A. Robinson, D. Cotton, R. White, K. A. Seffen, J. J. Baumberg, *Phy. Rev. Appl.* **2015**, 4, 044006.
- [35] F. Xu, Y. Zhu, *Adv. Mater.* **2012**, 24, 5117.
- [36] Z. Niu, H. Dong, B. Zhu, J. Li, H. H. Hng, W. Zhou, X. Chen, S. Xie, *Adv. Mater.* **2013**, 25, 1058.
- [37] M. Park, J. Im, M. Shin, Y. Min, J. Park, H. Cho, S. Park, M.-B. Shim, S. Jeon, D.-Y. Chung, J. Bae, J. Park, U. Jeong, K. Kim, *Nature Nanotech.* **2012**, 7, 803.
- [38] M. Park, J. Park, U. Jeong, *Nano Today* **2014**, 9, 244.
- [39] C. L. Choong, M. B. Shim, B. S. Lee, S. Jeon, D. S. Ko, T. H. Kang, J. Bae, S. H. Lee, K. E. Byun, J. Im, Y. Jeong, C. Park, J.-J. Park, U.-I. Chung, *Adv. Mater.* **2014**, 26, 3451.
- [40] M. Chen, T. Tao, L. Zhang, W. Gao, C. Li, *Chem. Commun.* **2013**, 49, 1612.
- [41] J. Yoon, S. Y. Hong, Y. Lim, S. J. Lee, G. Zi, J. S. Ha, *Adv. Mater.* **2014**, 26, 6580.
- [42] J. W. Boley, E. L. White, G. T. C. Chiu, R. K. Kramer, *Adv. Funct. Mater.* **2014**, 24, 3501.
- [43] J. Y. Sun, C. Keplinger, G. M. Whitesides, Z. Suo, *Adv. Mater.* **2014**, 26, 7608.
- [44] Z. Liu, M. Yu, J. Lv, Y. Li, Z. Yu, *ACS Appl. Mater. Interfaces* **2014**, 6, 13487.
- [45] Z. Liu, D. Qi, P. Guo, Y. Liu, B. Zhu, H. Yang, Y. Liu, B. Li, C. Zhang, J. Yu, *Adv. Mater.* **2015**, 27, 6230.
- [46] S. P. Lacour, J. Jones, S. Wagner, T. Li, Z. Suo, *Proc. IEEE* **2005**, 93, 1459.
- [47] A. Chortos, J. Lim, J. W. To, M. Vosgueritchian, T. J. Dussault, T. H. Kim, S. Hwang, Z. Bao, *Adv. Mater.* **2014**, 26, 4253.

- [48] H. Vandeparre, Q. Liu, I. R. Mineev, Z. Suo, S. P. Lacour, *Adv. Mater.* **2013**, 25, 3117.
- [49] H. L. Filiatrault, R. S. Carmichael, R. A. Boutette, T. B. Carmichael, *ACS Appl. Mater. Interfaces* **2015**, 7, 20745.
- [50] B. C.-K. Tee, A. Chortos, A. Berndt, A. K. Nguyen, A. Tom, A. McGuire, Z. C. Lin, K. Tien, W.-G. Bae, H. Wang, P. Mei, H.-H. Chou, B. Cui, K. Deisseroth, T. N. Ng, Z. Bao, *Science* **2015**, 350, 313.
- [51] S. Xu, Y. Zhang, L. Jia, K. E. Mathewson, K. I. Jang, J. Kim, H. Fu, X. Huang, P. Chava, R. Wang, *Science* **2014**, 344, 70.
- [52] J. Liang, L. Li, D. Chen, T. Hajagos, Z. Ren, S.-Y. Chou, W. Hu, Q. Pei, *Nat. Commun.* **2015**, 6, 7647.
- [53] J. Liu, T.-M. Fu, Z. Cheng, G. Hong, T. Zhou, L. Jin, M. Duvvuri, Z. Jiang, P. Kruskal, C. Xie, *Nat. Nanotechnol.* **2015**, 10, 629.
- [54] D.-H. Kim, N. Lu, R. Ma, Y. S. Kim, R. H. Kim, S. Wang, J. Wu, S. M. Won, H. Tao, A. Islam, *Science* **2011**, 333, 838.
- [55] I. R. Mineev, P. Musienko, A. Hirsch, Q. Barraud, N. Wenger, E. M. Moraud, J. Gandar, M. Capogrosso, T. Milekovic, L. Asboth, R. F. Torres, N. Vachicouras, Q. Liu, N. Pavlova, S. Duis, A. Larmagnac, J. Vörös, S. Micera, Z. Suo, G. Courtine, S. P. Lacour, *Science* **2015**, 347, 159.
- [56] D. Son, J. Lee, S. Qiao, R. Ghaffari, J. Kim, J. E. Lee, C. Song, S. J. Kim, D. J. Lee, S. W. Jun, *Nat. Nanotechnol.* **2014**, 9, 397.
- [57] Y. Shang, X. He, Y. Li, L. Zhang, Z. Li, C. Ji, E. Shi, P. Li, K. Zhu, Q. Peng, *Adv. Mater.* **2012**, 24, 2896.
- [58] C. Sealy, *Nano Energy* **2013**, 2, 325.
- [59] Z. M. Song, X. Wang, C. Lv, Y. H. An, M. B. Liang, T. Ma, D. He, Y. J. Zheng, S. Q. Huang, H. Y. Yu, H. Q. Jiang, *Sci. Rep.* **2015**, 5, 10660.
- [60] Z. Liu, D. Qi, P. Guo, Y. Liu, B. Zhu, H. Yang, Y. Liu, B. Li, C. Zhang, J. Yu, *Adv. Mater.* **2015**, 27, 6230.
- [61] Z. Niu, H. Dong, B. Zhu, J. Li, H. H. Hng, W. Zhou, X. Chen, S. Xie, *Adv. Mater.* **2013**, 25, 1058.
- [62] Y. Liu, H. Wang, W. Shi, W. Zhang, J. Yu, B. K. Chandran, C. Cui, B. Zhu, Z. Liu, B. Li, C. Xu, Z. Xu, S. Li, W. Huang, F. Huo, X. Chen, *Angew. Chem., Int. Ed.* **2016**, 55, 10660.

8884.

- [63] B. Zhu, H. Wang, W. R. Leow, Y. Cai, X. J. Loh, M. Y. Han, X.Chen, *Adv. Mater.* **2016**, 28, 4250.
- [64] Z. Liu, X. Wang, Q. Qi, C. Xu, J. Yu, Y. Liu, Y. Jiang, B.Q7 Liedberg, X. Chen, *Adv. Mater.* **2017**, 29, 1603382.
- [65] D. Qi, Z. Liu, M. Yu, Y. Liu, Y. Tang, J. Lv, Y. Li, J. Wei, B.Liedberg, Z. Yu, X. Chen, *Adv. Mater.* **2015**, 27, 3145.
- [66] Y. Sun, C. Keplinger, G. M. Whitesides, Z. Suo, *Adv. Mater.* **2014**, 26, 7608.
- [67] Z. Liu, M. Yu, J. Lv, Y. Li, Z. Yu, *ACS Appl. Mater. Interfaces* **2014**, 6, 13487.
- [68] C. F. Guo, T. Sun, Q. Liu, Z. Suo, Z. Ren, *Nat. Commun.* **2014**, 5, 3132
- [69] H. L. Filiatrault, R. S. Carmichael, R. A. Boutette, T. B.Carmichael, *ACS Appl. Mater. Interfaces* **2015**, 7, 20745
- [70] D. Vella, J. Bico, A. Boudaoud, B. Roman, P. M. Reis, *Proc.Natl. Acad. Sci. USA* **2009**, 106, 10901
- [71] J. Tang, J. Li, J. J. Vlassak, Z. Suo, *Soft Matter.* **2016**, 12, 1093
- [72] D. J. Lipomi, *Adv. Mater.* **2016**, 28, 4180
- [73] O. Graudejus, P. Go#rrn, S. Wagner, *ACS Appl. Mater. Interfaces* **2010**, 2, 1927
- [74] Z. F. Liu, S. Fang, F. A. Moura, J. N. Ding, N. Jiang, J. Di, M.Zhang, X. Lepro, D. S. Galv ' ao, C. S. Haines, ~ *Science* **2015**, 349,400.
- [75] D. S. Gray, J. Tien, C. S. Chen, *Adv. Mater.* **2004**, 16, 393.
- [76] F. Xu, Y. Zhu, *Adv. Mater.* **2012**, 24, 5117.
- [77] M. Park, J. Im, M. Shin, Y. Min, J. Park, H. Cho, S. Park, M.-B.Shim, S. Jeon, D.-Y. Chung, J. Bae, J. Park, U. Jeong, K. Kim, *Nat. Nanotechnol.* **2012**, 7, 803.
- [78] J. Yoon, S. Y. Hong, Y. Lim, S. J. Lee, G. Zi, J. S. Ha, *Adv.Mater.* **2014**, 26, 6580.
- [79] S. P. Lacour, J. Jones, S. Wagner, T. Li, Z. Suo, *Proc. IEEE* **2005**, 93, 1459.
- [80] K.-Y. Chun, Y. Oh, J. Rho, J.-H. Ahn, Y.-J. Kim, H. R. Choi, S.Baik, *Nat. Nanotechnol.* **2010**, 5, 853.
- [81] J. A. Fan, W.-H. Yeo, Y. Su, Y. Hattori, W. Lee, S.-Y. Jung, Y.Zhang, Z. Liu, H. Cheng, L. Falgout, M. Bajema, T. Coleman, D. Gregoire, R. J. Larsen, Y. Huang, J. A. Rogers, *Nat. Commun.* **2014**, 5, 3266.
- [82] P. Lee, J. Lee, H. Lee, J. Yeo, S. Hong, K. H. Nam, D. Lee, S.S. Lee, S. H. Ko, *Adv. Mater.* **2012**, 24, 3326.

- [83] C. F. Guo, T. Sun, Q. Liu, Z. Suo, Z. Ren, *Nat. Commun.* **2014**, *5*, 3121.
- [84] C. T. McKee, J. A. Last, P. Russell, C. J. Murphy, *Tissue Eng., Part B* **2011**, *17*, 155.
- [85] S. P. Lacour, G. Courtine, J. Guck, *Nat. Rev. Mater.* **2016**, *1*, 16063.
- [86] T. Saxena, J. L. Gilbert, J. M. Hasenwinkel, *J. Biomed. Mater. Res. A* **2009**, *90A*, 1206.
- [87] C. I. Buchanan, R. L. Marsh, *J. Appl. Physiol.* **2001**, *90*, 164.
- [88] R. G. Cutlip, K. B. Geronilla, B. A. Baker, M. L. Kashon, G. R. Miller, A. W. Schopper, *J. Appl. Physiol.* **2004**, *96*, 507.
- [89] E. J. Chen, J. Novakofski, W. K. Jenkins, W. D. O. Brien, IEEE Trans. Ultrason. FERR. 1996, 43, 191. Q8
- [90] A. Vinckier, G. Semenza, *FEBS Lett.* 1998, 430, 12.
- [91] A. Rauf, *IJSET* 2014, 3, 1419.
- [92] R. L. Lieber, J. Friden, *J. Appl. Physiol.* 1993, 74, 520.
- [93] Y. Huang, Y. Huang, W. Meng, M. Zhu, H. Xue, C.-S. Lee, C. Zhi, *ACS Appl. Mater. Interfaces* 2015, 7, 2569.
- [94] B. G. Vossen, P. J. Schreurs, O. van der Sluis, M. Geers, *J. Mech. Phys. Solids* 2014, 66, 117.
- [95] W.-S. Kim, I.-H. Yun, J.-J. Lee, H.-T. Jung, *Int. J. Adhes. Adhes.* 2010, 30, 408.
- [96] T. Sekitani, Someya T., *Mater. Today* **2011**, *14*, 398-407.
- [97] D.-H. Kim, Ghaffari R., Lu N., Rogers J. A., *Annu. Rev. Biomed. Eng.* **2012**, *14*, 113-128.
- [98] S. Jung, Lee J., Hyeon T., Lee M., Kim D. H., *Adv. Mater.* **2014**, *26*, 6329-6334.
- [99] C. Yan, Kang W., Wang J., Cui M., Wang X., Foo C. Y., Chee K. J., Lee P. S., *ACS nano* **2013**, *8*, 316-322.
- [100] S. Xu, Zhang Y., Jia L., Mathewson K. E., Jang K.-I., Kim J., Fu H., Huang X., Chava P., Wang R., *Science* **2014**, *344*, 70-74.
- [101] N. T. Tien, Jeon S., Kim D. I., Trung T. Q., Jang M., Hwang B. U., Byun K. E., Bae J., Lee E., Tok J. B. H., *Adv. Mater.* **2014**, *26*, 796-804.
- [102] M. Melzer, Mönch J. I., Makarov D., Zabala Y., Cañón Bermúdez G. S., Karnaushenko D., Baunack S., Bahr F., Yan C., Kaltenbrunner M., *Adv. Mater.* **2014**.
- [103] D.-H. Kim, Lu N., Ma R., Kim Y.-S., Kim R.-H., Wang S., Wu J., Won S. M., Tao

- H.,Islam A., *Science* **2011**, 333, 838-843.
- [104] M. Ramuz, Tee B. C. K., Tok J. B. H., Bao Z., *Adv. Mater.* **2012**, 24, 3223-3227.
- [105] A. Cirillo, Cirillo P., De Maria G., Natale C., Pirozzi S., *Sens. Actuators, A* **2014**, 212, 110-122.
- [106] T. IláLee, SoonáJang W., SangáKim Y., LináWang Z., KooáBaik H., *Energ. Environ. Sci.* **2014**, 7, 3994-3999.
- [107] J. Kim, Lee M., Shim H. J., Ghaffari R., Cho H. R., Son D., Jung Y. H., Soh M., Choi C., Jung S., *Nat. Commun.* **2014**, 5.
- [108] H. S. Song, Kwon O. S., Lee S. H., Park S. J., Kim U.-K., Jang J., Park T. H., *Nano Lett.* **2012**, 13, 172-178.
- [109] B. Zhu, Niu Z., Wang H., Leow W. R., Wang H., Li Y., Zheng L., Wei J., Huo F., Chen X., *Small* **2014**, 10, 3625-3631.
- [110] A. P. Gerratt, Sommer N., Lacour S., Billard A. In *Stretchable capacitive tactile skin on humanoid robot fingers-first experiments and results*, Proceedings of the IEEE International Conference on Humanoid Robots, **2014**.
- [111] H. Nakamoto, Oida S., Ootaka H., Tada M., Hirata I., Kobayashi F., Kojima F. In *Application of stretchable strain sensor for pneumatic artificial muscle*, Robotic Intelligence In Informationally Structured Space (RiSS), 2014 IEEE Symposium on, IEEE: **2014**; pp 1-5.
- [112] T. Yamada, Hayamizu Y., Yamamoto Y., Yomogida Y., Izadi-Najafabadi A., Futaba D. N., Hata K., *Nat. Nanotech.* **2011**, 6, 296-301.
- [113] D. Son, Lee J., Qiao S., Ghaffari R., Kim J., Lee J. E., Song C., Kim S. J., Lee D. J., Jun S. W., *Nat. Nanotech.* **2014**, 9, 397-404.
- [114] P. J. Mossop, McLachlan C. S., Amukotuwa S. A., Nixon I. K., *Nat. Clin. Pract. Cardiovasc. Med.* **2005**, 2, 316-321.
- [115] D. Gamez, Fidjeland A. K., Lazdins E., *Bioinspir. Biomim.* **2012**, 7, 025008.
- [116] D. J. Cohen, Mitra D., Peterson K., Maharbiz M. M., *Nano Lett.* **2012**, 12, 1821-1825.
- [117] X. Wang, Li T., Adams J., Yang J., *J. Mater. Chem. A* **2013**, 1, 3580-3586.
- [118] D. J. Lipomi, Vosgueritchian M., Tee B. C., Hellstrom S. L., Lee J. A., Fox C. H., Bao Z., *Nat. Nanotech.* **2011**, 6, 788-792.
- [119] Y. Shang, He X., Li Y., Zhang L., Li Z., Ji C., Shi E., Li P., Zhu K., Peng Q., *Adv.*

Mater. **2012**, 24, 2896-2900.

[120] L. Cai, Song L., Luan P., Zhang Q., Zhang N., Gao Q., Zhao D., Zhang X., Tu M., Yang F., *Sci. Rep.* **2013**, 3.

[121] J.-H. Kong, Jang N.-S., Kim S.-H., Kim J.-M., *Carbon* **2014**, 77, 199-207.

[122] M. K. Shin, Oh J., Lima M., Kozlov M. E., Kim S. J., Baughman R. H., *Adv. Mater.* **2010**, 22, 2663-2667.

[123] K. Liu, Sun Y., Liu P., Lin X., Fan S., Jiang K., *Adv. Funct. Mater.* **2011**, 21, 2721-2728.

[124] C. Pang, Lee G.-Y., Kim T.-i., Kim S. M., Kim H. N., Ahn S.-H., Suh K.-Y., *Nat. Mater.* **2012**, 11, 795-801.

[125] X. Xiao, Yuan L., Zhong J., Ding T., Liu Y., Cai Z., Rong Y., Han H., Zhou J., Wang Z. L., *Adv. Mater.* **2011**, 23, 5440-5444.

[126] F. Xu, Zhu Y., *Adv. Mater.* **2012**, 24, 5117-5122.

[127] S. Yao, Zhu Y., *Nanoscale* **2014**, 6, 2345-2352.

[128] F. Xu, Durham III J. W., Wiley B. J., Zhu Y., *ACS nano* **2011**, 5, 1556-1563.

[129] A. Chortos, Lim J., To J. W., Vosgueritchian M., Dusseault T. J., Kim T. H., Hwang S., Bao Z., *Adv. Mater.* **2014**, 26, 4253-4259.

[130] M. Park, Im J., Shin M., Min Y., Park J., Cho H., Park S., Shim M.-B., Jeon S., Chung D.-Y., *Nat. Nanotech.* **2012**, 7, 803-809.

[131] S.-H. Bae, Lee Y., Sharma B. K., Lee H.-J., Kim J.-H., Ahn J.-H., *Carbon* **2013**, 51, 236-242.

[132] Y. Wang, Yang R., Shi Z., Zhang L., Shi D., Wang E., Zhang G., *ACS nano* **2011**, 5, 3645-3650.

[133] C. Yan, Wang J., Kang W., Cui M., Wang X., Foo C. Y., Chee K. J., Lee P. S., *Adv. Mater.* **2014**, 26, 2022-2027.

[134] X. Li, Zhang R., Yu W., Wang K., Wei J., Wu D., Cao A., Li Z., Cheng Y., Zheng Q., *Sci. Rep.* **2012**, 2.

[135] M. Hempel, Nezhich D., Kong J., Hofmann M., *Nano Lett.* **2012**, 12, 5714-5718.

[136] S. Cheng, Wu Z., *Adv. Funct. Mater.* **2011**, 21, 2282-2290.

[137] N. Liu, Fang G., Wan J., Zhou H., Long H., Zhao X., *J. Mater. Chem.* **2011**, 21, 18962-18966.

[138] B. Sun, Long Y.-Z., Liu S.-L., Huang Y.-Y., Ma J., Zhang H.-D., Shen G., Xu S.,

Nanoscale **2013**, 5, 7041-7045.

- [139] M. Kollosche, Stoyanov H., Laflamme S., Kofod G., *J. Mater. Chem.* **2011**, 21, 8292-8294.
- [140] M. Li, Li H., Zhong W., Zhao Q., Wang D., *ACS Appl. Mat. Interfaces* **2014**, 6, 1313-1319.
- [141] J.-B. Chossat, Park Y.-L., Wood R. J., Duchaine V., *Sensors* **2013**, 13, 3405-3414.
- [142] J. Park, Wang S., Li M., Ahn C., Hyun J. K., Kim D. S., Kim D. K., Rogers J. A., Huang Y., Jeon S., *Nat. Commun.* **2012**, 3, 916.
- [143] J. T. Muth, Vogt D. M., Truby R. L., Mengüç Y., Kolesky D. B., Wood R. J., Lewis J. A., *Adv. Mater.* **2014**, 26, 6307-6312.
- [144] J. A. Rogers, Someya T., Huang Y., *Science* **2010**, 327, 1603-1607.
- [145] T. Yamada, Y. Hayamizu, Y. Yamamoto, Y. Yomogida, A. Izadi-Najafabadi, D. N. Futaba, K. Hata, *Nat. Nanotech.* 2011, 6, 296.
- [146] D. J. Lipomi, M. Vosgueritchian, B. C. Tee, S. L. Hellstrom, J. A. Lee, C. H. Fox, Z. Bao, *Nat. Nanotech.* 2011, 6, 788.
- [147] E. Roh, B. U. Hwang, D. Kim, B. Y. Kim, N. E. Lee, *ACS Nano* 2015, 9, 6252
- [148] S. Ryu, P. Lee, J. B. Chou, R. Xu, R. Zhao, A. J. Hart, S. G. Kim, *ACS Nano* 2015, 9, 5929.
- [149] R. Rahimi, M. Ochoa, W. Yu, B. Ziaie, *ACS Appl. Mat. Interfaces* 2015, 7, 4463.
- [150] X. Xiao, L. Yuan, J. Zhong, T. Ding, Y. Liu, Z. Cai, Y. Rong, H. Han, J. Zhou, Z. L. Wang, *Adv. Mater.* 2011, 23, 5440.
- [151] S. H. Bae, Y. Lee, B. K. Sharma, H. J. Lee, J. H. Kim, J. H. Ahn, *Carbon* 2013, 51, 236.
- [152] J. J. Park, W. J. Hyun, S. C. Mun, Y. T. Park, O. O. Park, *ACS Appl. Mat. Interfaces* 2015, 7, 6317.
- [153] J. B. Chossat, Y. L. Park, R. J. Wood, V. Duchaine, *IEEE. Sens. J.* 2013, 13, 3405.
- [154] H. Lee, B. Seong, H. Moon, D. Byun, *RSC Adv.* 2015, 5, 28379.
- [155] F. Xu, Y. Zhu, *Adv. Mater.* 2012, 24, 5117.
- [156] C. Pang, G. Y. Lee, T. I. Kim, S. M. Kim, H. N. Kim, S. H. Ahn, K. Y. Suh, *Nat. Mater.* 2012, 11, 795.
- [157] J. T. Muth, D. M. Vogt, R. L. Truby, Y. Mengüç, D. B. Kolesky, R. J. Wood, J. A. Lewis, *Adv. Mater.* 2014, 26, 6307.

- [158] S. P. Lacour, Chan D., Wagner S., Li T.,Suo Z., *Appl. Phys. Lett.* **2006**, 88, 204103.
- [159] K.-Y. Chun, Oh Y., Rho J., Ahn J.-H., Kim Y.-J., Choi H. R.,Baik S., *Nat. Nanotech.* **2010**, 5, 853-857.
- [160] Y. Kim, Zhu J., Yeom B., Di Prima M., Su X., Kim J.-G., Yoo S. J., Uher C.,Kotov N. A., *Nature* **2013**, 500, 59-63.
- [161] Z. Liu, Yu M., Lv J., Li Y.,Yu Z., *ACS Appl. Mat. Interfaces* **2014**, 6, 13487-13495.
- [162] L. Liu, Niu Z., Zhang L., Zhou W., Chen X.,Xie S., *Adv. Mater.* **2014**, 26, 4855-4862.
- [163] Z. Huang, Hong W.,Suo Z., *J. Mech. Phys. Solids.* **2005**, 53, 2101-2118.
- [164] G. M. Whitesides,Grzybowski B., *Science* **2002**, 295, 2418-2421.
- [165] X. Chen, Rogach A. L., Talapin D. V., Fuchs H.,Chi L., *J. Am. Chem. Soc.* **2006**, 128, 9592-9593.
- [166] H. Xu, Lu N., Shi G., Qi D., Yang B., Li H., Xu W.,Chi L., *Langmuir.* **2011**, 27, 4963-4967.
- [167] T.-S. Wong, Chen T.-H., Shen X.,Ho C.-M., *Anal. Chem.* **2011**, 83, 1871-1873.
- [168] Z. Zhang, Zhang X., Xin Z., Deng M., Wen Y.,Song Y., *Adv. Mater.* **2013**, 25, 6714-6718.
- [169] Q. Li, Zhu Y. T., Kinloch I. A.,Windle A. H., *J. Phys. Chem. B* **2006**, 110, 13926-13930.
- [170] H. Zeng, Kristiansen K., Wang P., Bergli J.,Israelachvili J., *Langmuir.* **2011**, 27, 7163-7167.
- [171] A. Shimoni, Azoubel S.,Magdassi S., *Nanoscale* **2014**, 6, 11084-11089.
- [172] Gray, D. S., Tien, J. and Chen, C. S. *Adv. Mater.* **2004**, 16, 393–397.

Chapter 3

Experimental Methodology

In this chapter, the principles behind the techniques used and the data analysis methods are discussed. The very first step is to fabricate the polymer substrate followed by surface modification for the subsequent film deposition either by thermal evaporation or by electrical deposition. The surface chemistry affects the film growth significantly. It has to be carefully engineered in the material design. The film growth is also carefully controlled according to the film growth principle. Island growth mode is preferred in this study. The mechanical and electrical testing are also introduced in this chapter, especially for the synchronous measurement of resistance and strain applied. Technologies of image, including optical and electron-based ones are also presented here. Data analysis is carried out by using Matlab and Imagej softwares.

3.1 Polymer substrate and active materials preparation

PDMS substrate was prepared by using spin coating. A silicon wafer was used as a rigid backing after hydrophobization treatment by applying 1H, 1H, 2H, 2H perfluoro-octyl-trichlorosilane. The prepolymer and cross linker were mixed together in a 10:1 ratio after defoaming by vacuum, then spun at 600 rpm, sixty seconds, finally cured it in 80 °C for three hours. The final thickness of around 110 micrometers film was obtained. The hollow mask was fabricated by photolithography method. The mask was for fabricating hydrophilic locations on PDMS. It was fabricated by utilizing customized equipment and the copper foil with the thickness of around 10 micrometers was taken as the substrate to be covered with one layer of photoresist at 3000 rpm for 60 seconds. After that, it was made by standard photoetching method. The thin copper film was etched by 1 mol/L solution of FeCl_3 . And then it was cleaned by using deionized water with the help of ultrasound for five mins, dried in 60 °C oven for thirty mins and then adhered to the substrate accordingly. Finally, the oxygen plasma was applied with pressure of five mbar and power of 50 W for one minute.^[1-5]

The SWCNTs with carboxylic functional group can be dispersed easily in the ultrasound bath. It could be used after around ten minutes standing to get down the large aggregates. The concentration of two gram per liter was utilized here. Finally, the fabricated sensors were ready to be used (Figure 3.1).

Figure 3.1 The thickness-gradient film fabricated by using the self-pinning effect. a, The liquid level is pinned for the most of the evaporation time resulting in gradient structure. During the process, there would be the hydrogen bond between the carboxylic acid groups on carbon nanotubes and the hydroxyl groups on PDMS improving the adhesion. b, The original resistance of typical sensors with different plasma power for the hydrophilization treatment of PDMS substrate.

The PDMS film could be tuned to around 50 μm thickness by using proper spinning speed. The PDMS ring was made on the half-cured PDMS thin film. The thin PDMS film could be free-standing by using this method after being cured in 80 °C for three hours. A hole with around 30 mm in diameter was made at center in a Petri dish and then covered by the fabricated free-standing thin film.

Preparation of e-hair template and stiffener. The template was 3D printed using Ultimaker 2 with the nozzle diameter of 0.4 mm and the printed polymer was polylactic acid (PLA). The rigid part of PLA (around 15 mm in length) with the tensile modulus of 3.5 GPa was taken as the stiffener inside the hair. In order to make stretchable e-hair hollow, the template had a cone-shaped root with the diameter of 7 mm for the base circle and the height of 5 mm. The diameter of the e-hair is around 1.8 mm in cylindrical shape.

Preparation of stretchable e-hair. The polydimethylsiloxane (PDMS), purchased from Sigma Aldrich, was employed as the soft substrate. The prepolymer and the cross linker were mixed together in a ratio of 10:1 by weight, and then defoamed by vacuum for about half of an hour, finally dropped onto the e-hair template fully, then spin coated at 500 rpm for 60 s and cured in 60 °C for 6 h. The thickness of the PDMS film was about 320 μm . The SWCNTs modified with the hydrophilic function group of carboxylic acid was from Carbon Solution, Inc.. It was dispersed in the deionized water in ultrasound water bath. The power was 200 W for about 2 hours (Fisher Scientific FB15051). The SWCNTs with the concentration of 2 g L⁻¹ can be well dispersed in the solution and ready to be used after around 15 minutes' standing for the subsiding of the large aggregates.

Next, the gradient root of the e-hair was exposed to the oxygen plasma to become hydrophilic by using a covering mask with circled hollow pattern to limit the hydrophilic area. The oxygen pressure was 5 mbar with power of 50 W for 0.5 minute. After removing the hollow mask, 10 μL SWCNT solution was dropped on the gradient root and immediately covered the pattern even climbing up the hair to the height of about 2 mm under the assistance of capillary force. After the evaporation for around 30 minutes in the air at room temperature, the 3D self-pinning effect ended. Finally, the e-hair was cut off from the PLA substrate with the stick left inside the hair, and the e-hair was ready to be tested after the careful encapsulation (Figure 3.2). The stretchable e-hair array was also prepared in this similar method. However, the wire bonding was more complicated and performed among the e-hairs following the pattern of crossing bar, and then the resistance vibration of certain hair was calculated by solving the linear equations.

Figure 3.2 Flow diagram of e-hair fabrication. a, 3D printed mould with polylactic acid (PLA). b, PDMS film is coated on it. c, Cutting off with the stiffener stick inside. d, Partial hydrophilization with oxygen plasma. e, CNT solution is dropped on covering the whole root and part of the hair body under the help of capillary force. f, Out-of-plane multiple rings form on the hair body and root by 3D self-pinning effect.

Fabrication of PDMS fibers: PDMS 184 (Sigma Aldrich) with 1:10 weight ratio of the prepolymer and the cross linker was prepared following the normal procedure, and then pre-cured in 60 °C oven for around 25 minutes, lastly, kept in room temperature for different time to obtain the PDMS with different viscosity. Meanwhile, the clean silicon oil was heated up to 170 to 180 degree centigrade. During this process, it should be emphasized that the more uniform the temperature field of the silicon oil is, the better the quality of the fiber is, because the micro fibers were cured within 3 seconds in the hot oil and the temperature vibration would induce different thermal expansion in the same fiber inducing the abnormal deformation. When the oil bath was ready, certain amount of PDMS precursor was stretched in a short time and then put into the bath. After few seconds, the fiber was ready and taken out followed by the washing process by using daily-used cleaning fluid of hand sanitizer and deionized (DI) water. Finally, fibers were immersed in the DI water overnight and then dried in 60 °C oven.

Fabrication of beads onto the fibers: the prepared PDMS fibers were used to further do the modification with PDMS beads. The viscosity tuning process of the PDMS precursor was the same with that described in the fabrication of the fiber. Then fibers were immersed into the precursor for few seconds and then suspended vertically along the length direction. After tens of seconds, beads will appear and then the fiber with beads

was put into the hot oil following the same process described before. The beads diameter could be further regulated by using the PDMS precursor with different viscosity.

Fabrication of the stretchable gold film and carbon nanotube film onto the fiber:^[6-10] In order to demonstrate that the beads-on-fiber PDMS can act as the platform to enhance the sensitivity of the strain sensor, two kinds of stretchable conductive materials were employed as the active layer. One was the stretchable gold film reported by the previous study; this film was with initial nano cracks without strain applied and these nano cracks will grow into micro cracks releasing the strain in the first strain cycle. Then subsequently, micro cracks opened and closed during the next strain cycles inducing the resistance change and achieving the stretchability of the gold film. The other one was the stretchable carbon nanotube film reported by the previous study. This film followed the same principle to achieve the stretchability. MTS model 42 was employed to apply the tensile strain. And the liquid metal (Gallium-indium eutectic, Aldrich) acted as the wire bonding adhesive which could surface the tensile strain. Keithley 4200-SCS was used to do the measurement using a sampling rate of 125 samples per second.

Figure 3.3 Schematic diagram of the strategy of dynamic interface mingling and corresponding physical analyses. a) Diagram illustrating to show the fabrication process and uncured PDMS was used as the substrate to receive the evaporated gold. b) Physical models of heat transfer and viscous flow during the dynamic process. c) Simulation results of the temperature distribution in the film and corresponding pressure distribution during the viscous flow under different viscosity (low viscosity in left and higher in right). d) Diagram of the unique self-stripping double-layer structure.

Fabrication of high-performance stretchable conductors: Glass slides without any pre-treatment worked as the rigid backing for uncured PDMS (184, Dow Corning) with different ratio of cross linker to monomer of 1:5, 1:10, 1:20 and different pre-curing time of 15, 20, 25 minutes, respectively, in the 60 °C oven . The sample was pasted onto the trial of the thermal evaporation machine with the PDMS film facing down towards the gold source. When the vacuum achieved to 1.0×10^{-6} Torr, the chromium and gold source was heated up and started to evaporate in sequence at the rate of 0.2 and 0.5 Å s⁻¹, respectively. The sample was ready after the evaporation (Figure 3.3).

Preparation of normal stretchable and flat non-stretchable gold film: As control samples, films were prepared following the previous method. The normal crack-based stretchable gold film had an appearance of brown color due to the thin film thickness required by the special morphology of initial nano cracks. The thickness of the film was around 80 nm. The up limit of the thickness for this stretchable film was around 100 nm.

Peel test of tensile adhesion strength: The strength was obtained following the classical test process. The cylindrical wood sticks were well adhered to samples by epoxy resin. MTS C42 with 50 N load cell was employed to test the adhesion force when the stick was pulled up by the Bionix vice grips. Moreover, the synchronous measurement of resistance and tensile strain was performed as reported previously.^[1]

3.2 Surface modification

After the surface modification, CNT solution was dropped onto the PDMS substrate. This modification was to make the surface hydrophilic. The method is to used oxygen plasma or air plasma to hit the surface of the PDMS. The function group will be replaced with hydrophilic ones. Figure 3.4 illustrates the liquid state when the CNT solution was dropped onto the hydrophilic surface.

a 3D printing substrate

b Coated with PDMS

c Peeling off with stiffener inside

d Partial hydrophilization with O_2 plasma

e Dropping CNT solution

f Evaporating and multi rings formation

Figure 3.5 3D coffee ring effect after proper surface modification onto the 3D structure.

3.3 Film deposition technologies

For CNT film deposition, the coffee ring effect was employed. The typical bundle of

CNT is around 1 μm in length and 100 nm in diameter. These small particle-like structures can be driven by the gradient evaporation rate on top of the liquid surface (Figure 3.6). And finally, the ultra-thin film of CNT can be fabricated in the central area, and there is a thick film at the edge.

Figure 3.6 Thin film with gradient thickness by coffee ring effect.

By simply tuning the construction of the boundary, the ring formation can be well controlled. For example, if the two side edges of the film are orthogonal, and the solution is dropped in the corner, there will be multiple rings generated (Figure 3.7). These multiple rings could also be used to tune the sensitivity of the stretchable strain sensor.

Figure 3.7 Multiple rings formation only by folding the substrate film. a, Diagram of the method of multi-ring formation. The PDMS substrate is folded, then made hydrophilic, and finally dropped with CNT solution in the corner. b, Image of fabricated multi-ring SWCNTs film. Red dash line illustrates the central line of the corner.

For the growth of metal film by atoms stacking, it is well known that there are mainly

three modes here (Figure 3.8). The bottom two are preferred for fabricating stretchable metal film, because there would be initial defects generated. But for this strategy, this stretchable film would be the control samples. And this strategy will not depend on the growth mode of the metal film, but the strain distribution will be regulated by proper designs.

Figure 3.8 Three thin film growth modes for metal film by atoms stacking.

Figure 3.9 Diagram to illustrate the fabrication process of stretchable gold film with nanopiles. The green color shown for the Cu tape represents the adhesive material on the Cu film that is totally transferred to gold film after peeling off the sample from the Cu tape indicating the good adhesion of the sample.

Fabrication of high-adhesion stretchable electrodes and sensors: AAO templates purchased from Whatman, Singapore and Puyuan Nano, China with the pore size of around 100 nm were directly thermally evaporated with gold film of different thickness from 30 nm to 500 nm without any pre-treatment. The vacuum was around 1.5×10^{-6} Torr, the evaporation rate was $0.5 \text{ \AA s}^{-1}$ and the distance from the gold source to the target was around 8 cm. The target tray rotated in 10 rpm. Then, the template, as the working electrode and with Pt and Ag/AgCl as the counter and reference electrodes, was electro-deposited with gold nanopile with different length by controlling the deposition time. The electroplating solution was the commercialized Au Orotemp 24 (Technic Inc.) and the potential bias used was -0.95 V. After that, AAO templates were adhered with Cu tape and then adhered to the glass petri dishes by double-side carbon tape. AAO templates were removed by 3 mol L^{-1} NaOH solution completely followed by DI water washing and natural drying. The PDMS with the 1:10 weight ratio of the cross linker and monomer was diluted with hexane. The weight ratio of PDMS and hexane was 3:7. The pervious samples underwent oxygen plasma treatment and then were poured with the diluted PDMS immediately. The samples were put into vacuum for two hours when the diluted PDMS gradually went into the gaps among the nanopiles and hexane evaporated away at the same time. Lastly, they completed the polymerization in the oven at $80 \text{ }^{\circ}\text{C}$. Fabricated samples can be peeled off from the Cu tape with the adhesive materials transferred from Cu film to the gold film which already indicated the good adhesion achieved (Figure 3.9).

3.4 Synchronous testing of electrical and mechanical signals

Dynamic resistance measurement: Instron 5848 was used to apply uniaxial strain. Liquid was employed metal to connect with the sensor. Keithley 4200-SCS was used to measure the resistance. There are two methods to do the testing: one is the manual (Figure 3.10) and the other is the automatic (Figure 3.11).

Figure 3.10 Thickness-gradient stretchable gold film with initial nanocracks. a) The film was stretched by using a customized stretcher. b) Optical images of the film under different strain. c) The gauge factor enhancement by applying the proposed new strategy.

Figure 3.11 Dynamic stretching with resistance testing. The dynamic stretcher is at left side and the right shows the resistance testing equipment.

The load cell of 500 N was used to test the tensile force by employing mechanical tester MTS C43. The tensile speed was 1- 10 mm/min. The cyclic bending strain was also applied by using this machine and a customized transducer to change the vertical displacement to rotation. Field emission scanning electron microscopy (FESEM) was

performed using JEOL 7600F with the accelerating voltage of 5 kV and the current of 110 pA. The resistance was measured by using Keithley 4200-SCS with the sampling rate of 125 points per second.

The bonding copper wires were with diameter of 0.1 mm to make the compliant contact with the SWCNTs rings (Figure 3.12). The liquid metal (Gallium-Indium eutectic, Aldrich) served as the conductive adhesive for hugely improving the stability of this encapsulation, especially benefitting the dynamic resistance testing. It should be emphasized that wires were all shaped in an arc to keep continuous contact during the cyclic loading.

Figure 3.12 Image to show five-point encapsulation method (a) side view and (b) top view. Herein, liquid metal, with high mobility and surface tension which is ideal for flexible encapsulation, is employed to connect the sensing film with the bonding wires.

Nitrogen was employed here to apply the gas flow of different speed. The double faced adhesive tape was used to modify on the head of the e-hair to enhance the gas pressure receiving. Gas gun was open first, applied nitrogen for around 1 second and then removed (Figure 3.13). The e-hair would suffer the damping vibration process before

reaching to the static state at last. The rubber tube with diameter of 5 mm was utilized to tune the different flow state by adjusting the tap pressure. Additionally, Reynolds number is the standard dimensionless number reflecting the flow state, and when it is larger than 4000, the flow state is usually taken as turbulence.

Figure 3.13 Air and water flow detection. a, Image to illustrate the detection of wide-range speed of nitrogen gas flow by tip-modified e-hair. b, Image to present the setup of detecting water flow. Diameter of the tube is 5 mm.

EMG signal and the deformation induced by the elbow bending were measured at the same time all by the fabricated stretchable units. Two working electrodes were placed on the biceps and one reference electrode was hold in hand. Two ends of the stretchable strain sensor were adhered to two sides of the elbow. EMG signal was amplified and pre-treated by the commercialized device and software (*Backyard Brains*).

3.5 Mechanical simulation

Mechanical simulation is a powerful tool to investigate the mechanical behavior when the experiment is not easy to conduct, e.g., the mechanical behavior at the micro scale. The simulation results could provide the design inspiration and suggest the material choice. For the thin film with nanopiles and without (Figure 3. 14), the difference can be observed very clearly. Also, for the micro pillars under the whole film, the strain regulation effect is also studied by this simulation (Figure 3.15).

Figure 3.14 FEM simulation of the film with nanopiles underneath and without.

Figure 3.15 FEM simulation model and results. a) Model of the substrate with randomly oriented micro pillars. b) The strain regulation effect induced by the micro pillars.

3.6 Image and data analysis

Commercial software Matlab, Origin, and the open-code software Imagej were utilized to analyze and visualized the data.

References:

- [1] Z. Liu, M. Yu, J. Lv, Y. Li, Z. Yu, *ACS Appl. Mater. Interfaces* **2014**, 6, 13487.
- [2] Z. Liu, D. Qi, P. Guo, Y. Liu, B. Zhu, H. Yang, Y. Liu, B. Li, C. Zhang, J. Yu, *Adv. Mater.* **2015**, 27, 6230.
- [3] S. P. Lacour, J. Jones, S. Wagner, T. Li, Z. Suo, *Proc. IEEE* **2005**, 93, 1459.
- [4] A. Chortos, J. Lim, J. W. To, M. Vosgueritchian, T. J. Dusseault, T. H. Kim, S. Hwang, Z. Bao, *Adv. Mater.* **2014**, 26, 4253.
- [5] H. Vandeparre, Q. Liu, I. R. Mineev, Z. Suo, S. P. Lacour, *Adv. Mater.* **2013**, 25, 3117.
- [6] J. T. Muth, D. M. Vogt, R. L. Truby, Y. Mengüç, D. B. Kolesky, R. J. Wood, J. A. Lewis, *Adv. Mater.* 2014, 26, 6307.
- [7] S. P. Lacour, Chan D., Wagner S., Li T., Suo Z., *Appl. Phys. Lett.* **2006**, 88, 204103.
- [8] X. Wang, Li T., Adams J., Yang J., *J. Mater. Chem. A* **2013**, 1, 3580-3586.
- [9] D. J. Lipomi, Vosgueritchian M., Tee B. C., Hellstrom S. L., Lee J. A., Fox C. H., Bao Z., *Nat. Nanotech.* **2011**, 6, 788-792.
- [10] Y. Shang, He X., Li Y., Zhang L., Li Z., Ji C., Shi E., Li P., Zhu K., Peng Q., *Adv. Mater.* **2012**, 24, 2896-2900.

Chapter 4

Coffee ring effect of carbon nanotubes*

Stretchable strain sensors are vital for the emerging soft electronics, including wearable and implantable devices, human-like robots with artificial skins, and bionic sensory systems. Particularly, the gauge factor (GF), reflecting the sensitivity, is vital for detecting the micro strain. High gauge-factor sensors can largely improve the threshold detection level, thus opening up for exploration of subtle strain phenomena. Several kinds of stretchable strain sensors were fabricated before, however, it remains a challenge to couple large stretchability with high sensitivity, because large stretchability demands that the material remains structurally and morphologically intact under large strain, while high sensitivity requires substantial structural changes even under small strain. In this work, for the first time, a new strategy was proposed by constructing the film with gradient thickness, which couples the seemingly contrary properties of brittleness and stretchability together to fabricate strain sensors with high gauge factor and large stretchability. The thickness-gradient film was formed by employing self-pinning effect of the single wall carbon nanotube solution. The fabricated sensor possesses surprisingly good performance covering all requirements of the sensitivity, stretchability and long-term stability.

*Published substantially as Liu et al., Thickness-gradient Films for High Gauge-factor Stretchable Strain Sensors, *Adv. Mater.* **2015**, 27, 6230.

4.1 Introduction

Stretchable strain sensors are critical for the mechanical feedback to the bio-system and would be the important part for the wearable sensors and even the implantable sensors. Recent years witness the rapid development of stretchable strain sensors made by all kinds of new materials, including nanoparticles, nanowires, nanoflakes and so on.^[1-50] But since either the fabrication method is complicated or the performance is not stable enough, the sensors still need to be further optimized to achieve the stable performance and go into people's daily life.^[51-61]

Herein, the mechanism of adjusting gauge factor is proposed through further investigating the principle behind the stretchability of rigid films on soft substrates, and then a new strategy, thickness-gradient films, was proposed to fabricate SSSs with all of those high performances based on single wall carbon nanotubes by employing self-spinning method, and this method is easy to be spread by using other materials. The novel SSSs can withstand uniaxial strain of more than 150%, isotropic strain of more than 75% (ϵ_A), and strain cycles of about 100,000 cycles and 20,000 cycles with 60% and 100% strain applied, respectively. More importantly, the sensitivity is highly improved, and the gauge factor (GF) achieves to about 51 and 5 when ϵ is less than 15% and more than 25%, respectively. With those high performances and the facile fabrication method, the high-performance SSSs, as partially demonstrated in this paper, can be potentially fabricated in large scale and extensively used in gait analysis, sound detection, micro-vibration and micro strain monitoring. Also, following the new strategy proposed here, different methods could be developed to fabricate the high-performance SSSs.

Figure 4.1 The inspiration of gradient structure from Golden Gate Bridge. The force is transferred step by step from the most fragile part without supporting points to the main tower, by using the gradient suspended cable. Inspired by it, the thickness-gradient film for high-gauge-factor stretchable strain sensor is proposed.

According to the definition of GF , the brittle conductive materials have the most high GF , because when applied a relatively small strain, $\varepsilon \rightarrow 0$, it will break, $\Delta R \rightarrow \infty$ and $GF = (\Delta R / R_0) / \varepsilon \rightarrow \infty$, but brittle materials do not have stretchability and its fracture is irreversible. Thus the sensor would possess both high stretchability and high sensitivity, if the brittleness could be combined with the stretchability. It seems hard to combine those contradictory properties. As a matter of fact, many nature objects have their own strategies to overcome this problem. Take a tree for example, from soft soil to its rigid body, it stands firmly by numerous roots into the soil forming a kind of gradient structure below the ground. Also, as for the artificial building, such as the Golden Gate Bridge, force is transferred from the fragile part without supporting locations to the main tower by the gradient suspension cable (Figure 4.1). So, inspired by them, the strategy of the gradient construction should be used.

Figure 4.2 Thickness-gradient films for obtaining high gauge factor and high stretchability. a,b) Demonstration images and FEM simulation showing the mechanism behind the property of stretchability of the rigid films on soft polymers, one piece of note paper on air in a), and strain energy is released by the wrinkles. Another one is fixed on a substrate, there would be no wrinkles and the throughout crack appears when the tensile strain applied in b). Based on the principle of the stretchability, the 3D image in c) with the desired structure would possess both high stretchability and high gauge factor.

As a start, the principle of stretchability of SSSs should be investigated first. Several strategies were proposed to achieve the stretchability.⁶²⁻⁶⁷ For a rigid film as illustrated in Figure 4.2a and b, it can be stretchable as suffering tensile strain when strain energy is released by the wrinkles. Here, wrinkles could be seen as the spring, however, if the rigid film is fixed on the substrate when applied strain and no wrinkles form, i.e., the wavelength of wrinkles is infinite, the strain energy can only be released by the propagation of the crack, and this process decreases the stretchability significantly, but greatly increases GF as analyzed above. The finite element modeling analysis also proves that the strain concentration at the tip of crack in wrinkle structure is about 40% smaller than that in flat film as shown in Figure 1a and b. Therefore, if the wavelength of wrinkles can be regulated, combining the large-wavelength-wrinkle structure together with that with smaller wrinkles will endow one sensor with both high stretchability and large GF . Furthermore, according to the buckling theory of rigid film on soft substrates, the

wavelength is as following:⁶⁸

$$\lambda = 2\pi h \left(\frac{\bar{E}_f}{\bar{E}_s} \right) \quad (1)$$

where h is the thickness; $\bar{E}_f = E_f / (1 - \nu_f^2)$, $\bar{E}_s = E_s / (1 - \nu_s^2)$ are the plane strain moduli, and E_f , ν_f , E_s , ν_s are modulus and Poisson's ratio. So if the film has gradient thickness, there would be gradient wavelength when applying tensile strain (Figure 4.2c).

4.2 Experimental Methods

4.2.1 Carbon nanotubes solutions preparation

The PDMS substrate was prepared by using spin coating. A silicon wafer was used as a rigid backing after hydrophobization treatment by applying 1H, 1H, 2H, 2H perfluorooctyl-trichlorosilane. The prepolymer and cross linker were mixed together in a 10:1 ratio after defoaming by vacuum, then spun at 600 rpm, sixty seconds, finally cured it in 80 °C for three hours. The final thickness of around 110 micrometers film was obtained. The hollow mask was fabricated by photolithography method. The mask was for fabricating hydrophilic locations on PDMS. It was fabricated by utilizing customized equipment and the copper foil with the thickness of around 10 micrometers was taken as the substrate to be covered with one layer of photoresist at 3000 rpm for 60 seconds. After that, it was made by standard photoetching method. The thin copper film was etched by 1 mol/L solution of FeCl₃. And then it was cleaned by using deionized water with the help of ultrasound for five mins, dried in 60 °C oven for thirty mins and then adhered to the substrate accordingly. Finally, the oxygen plasma was applied with pressure of five mbar and power of 50 W for one minute.

The SWCNTs with carboxylic functional group can be dispersed easily in the ultrasound bath. It could be used after around ten minutes standing to get down the large aggregates. The concentration of two gram per liter was utilized here. Finally, the fabricated sensors were ready to be used.

4.2.2 Coffee ring formation process

Figure 4.3 Self-spinning to fabricate thickness-gradient stretchable strain sensor. a) Fabrication process of the CNTs film by self-spinning effect. b) Tensile strain of 60% is applied by using a stretcher. c) The microscope image of the thick part. The thick, transitional and thin regions could be approximately located and divided by red dot lines, the surface morphology of which are presented in d), e) and f) respectively. And the wavelength of wrinkles is measured. It decreases from the thick to the thin region as shown in g), which illustrates the gradient thickness of the film according to buckling theory.

In nano scale, it is quite difficult to fabricate specific patterns, but self-assembling process can be used to get them.^[69-71] Self-spinning process driven by the solution evaporation will be helpful to fabricate desired films.^[72-77] Generally, self-spinning process will take most of the time building up the thicker outer ring (Figure 4.3a).⁷⁸ Through this method, the fabrication process of the thickness-gradient single-wall carbon nanotubes (SWCNTs) film on elastic substrate of polydimethylsiloxane (PDMS) was proposed (Figure 4.3a). The SWCNTs were water soluble modified with carboxylic acid. The PDMS surface was hydrophobic originally, but could be changed to be hydrophilic by proper oxygen plasma treatment. By using desired exposure pattern in the mask, there would be certain area of hydrophilic region, like an “S” shape shown in Figure 4.3a. The film with various shapes can be fabricated through this facile method. Additionally, the hydrogen bond could be formed between the hydroxy, generated by the plasma treatment on PDMS, and the carboxylic acid modified on SWCNTs improving the adhesion of the film on PDMS.

Figure 4.4 Surface morphology of the ring region under tensile strain of 5%. Low- a) and high- b) magnification of FESEM images of the thick ring part. The thickness is increased from region I to IV sharply reflected by the crack size and wrinkle wavelength.

A sample fabricated by this method under 60% uniaxial strain is presented in Figure 2b and c. The thick part of the film is black and the inner thin part is transparent. When applied only 20% uniaxial strain, the throughout cracks exist in the thick ring region (Figure 4.4a) and even under 10% strain, it is nearly broken (Figure 4.4b). Detailed investigation on the wavelength changing from the thick region to the thin one is shown in Figure 4.3d-f. The width of the cracks in the thick region is much larger than that in

transitional and inner regions, in which the cracks are more random and interconnected. Further, the wavelength of the wrinkles is gradually reduced by over two orders of magnitude from outer to inner (Figure 4.3f). According to Equation 1, it indicates that the gradient-thickness film is successfully fabricated. The surface profile data in Figure 4.4a also proves this point and although the transitional region is only about 100 μm in width, it plays a key role in connecting the rigid thick part with the inner stretchable part. It can be seen that the throughout cracks in the thick region will branch in the transitional part and then merge with the numerous micro cracks in the inner thin region (Figure 4.4b). Also, the average thickness of the thick region is about 210 nm and that of the thin region is about 38 nm. Additionally, the detailed surface morphology confirms the proposed stretchability mechanism which predicts that the edge of the crack would suffer the out-of-plane bending (Figure 4.2a). It can be observed clearly in Figure S4b that there are protuberances at the edge of cracks that is also proven by the profile data (Figure 4.5).

Figure 4.5 The 3D and 2D surface morphology of the thin region under 60% strain.

4.3 Principal Outcomes

4.3.1 Both high stretchability and sensitivity achieved

Figure 4.6 Coffee ring effect to fabricate SSSs with gradient thickness. a) Schematic of coffee ring process of SWCNTs film. b) The gradient thickness data of the film. c) One sample under stretch of the tensile strain of 60% by a customized stretcher. d) The optical image of the ring region in c). The wavelength of wrinkles differs from the thin to the thick region as shown in e). The thickness could be divided into four regions marked with four capitalized Roman numbers. SEM images to show the surface morphology of the thin, gradient and thick regions are presented in f), g) and h).

Figure 4.7 Stretchable strain sensor performance when applied with uniaxial strain. a) PDMS substrate tends to break, when the applied tensile strain is larger than 150%. b) The stability of the sensor. The sensor keeps stable performance during the 100,000 strain cycles and the strain rate is 400 mm/min. Besides, it shows stable performance when 100% strain is applied in c). d) The gauge factors at different cycles. As presented in b), there are two linear regions when applied strain is less than 15% and larger than 25%. Two gauge factors can be calculated.

The fabricated SSSs and related characterizations are illustrated in Figure 4.6 in detail. The novel SSSs shows surprisingly good performance under uniaxial and isotropic strain which is quite vital for the practical application because the sensor will unavoidably suffer the multi-dimensional strain in practice. The strain rate of 10 mm/min was applied in order to eliminate the viscoelastic effect testing the intrinsic stretchability of the SSSs. The thickness of the PDMS substrate is about 110 μm , and under the uniaxial tensile strain of 150%, it tends to break first, which determines the stretchability of the sensor (Figure 4.7a) and meanwhile indicates that the stretchability of thickness-gradient SWCNTs film is much higher than that of normally used stretchable gold film.⁸⁵ More importantly, the testing of the durability shows that the SSSs can suffer 60% strain of 100,000 cycles, 100% strain of 20,000 cycles where PDMS substrates tend to break, and still have rather stable performance (Figure 4.7b and Figure 4.8a). The original data at

around 100,000 cycles under 60% strain and 20,000 strain under 100% is presented in Figure 4.8b and Figure 4.7c respectively. This durability is one of the best in reported SSSs, which hugely improves the service life taking a solid step towards the real application of SSSs. Besides, this novel SSSs still works in high temperature of up to 120 °C as shown in Figure 4.8c and due to the high thermal expansion coefficient of PDMS, the resistance response curve becomes lower but still keeps the changing characteristics which can be adjusted with certain calibration in practice.

Figure 4.8 The control experiment to present the importance of the thick part for the gauge factor improvement. a) The amplified present of the resistance changing before 15% strain. b) The resistance changing under the cyclic strain of 100% (20,000 cycles). c) The detailed data after applying 60% uniaxial strain of 100,000 cycles. d) The resistance changing under different temperature at 100% uniaxial strain.

Further, it is obvious in Figure 4.7b that there are mainly two lineal regions for this SSSs which is similar with that fabricated by another group, and the amplified curve for the small strain region is shown in Figure 4.8d. The gauge factor is rather high achieving to

about 51 in the first linear region before 15% strain and about 5 after 25% strain, which is quite suitable for the real application, because the high sensitivity is definitely needed for the small strain detection, but for the high strain, it is easy to induce lower signal-to-noise ratio if the sensor has too high sensitivity. The two phases of high gauge factor is induced by the gradient structure. As analyzed above, when the small strain of about 15% is applied, the thick ring region is totally broken, after that, the stretching process is dominated by the thin region. As a control experiment, the thick ring region was cut off and then the sample went through the exactly same testing process as described before (Figure 4.9). The GF decreases dramatically from 51 to only 2.8 indicating the importance of the gradient structure for the gauge factor improvement. The gauge factor of 51 achieved here is a breakthrough for the SSSs, hugely improving the sensitivity of the sensor, and based on it, as demonstrated below, very tiny vibration strain can be detected which will give more feedback information and extend the application field for the SSSs. More excitingly, following the principle proposed here, there is still more space for enlarging the gauge factor as desired by enlarging the thick region. Also, according to the Equation 1, people can carry out the principle from other perspectives such as adjusting the modulus properly.

Figure 4.9 The control experiment to present the importance of the thick part for the gauge factor improvement. For the control sample, the thick ring part was cut off.

The gauge factor is independent on how wide it was cut in theory, because gauge factor refers to the relative variation in the resistance. As shown in Figure 4.6c, the width of the ring is about 3 mm originally, so it is convenient to cut the lateral ring of around 200 μm in width by using sharp thin blade (the cutting edge is around 20 μm in width). And then the film was attached firmly on the PDMS substrate with standard testing shape (Figure 4.9) and applied tensile strain by fixing double-layer sample in order to minimum

the error of the strain transfer between the attached substrate and the sensor. Additionally, the testing strain is only 2%, under which it is reasonable to omit the dissymmetry of the strain distribution in the sensor. The result shows that when the thick region is cut off and then the 2% strain is applied, the gauge factor decreases dramatically from 161 to 2.8.

4.3.2 Isotropic stretchability

As mentioned above, the isotropic stretchability of the SSSs plays a critical role in the real application process. On the one hand, it prevents the damage for uniaxial strain detection from the unavoidable or occasional multi-dimensional strain; on another hand, it provides the possibility for the sensor to detect the inflation and shrinking process such as the strain monitoring of implanted artificial blood vessels to mechanically test the blood interaction with the artificial tissue. In order to apply the isotropic strain, the special customized setup was designed based on the reported method (Figure 4.10a-c).

The FEM simulation for the inflation process was applied to locate the strain concentration area where the SSSs was placed to be tested as shown in Figure 4.10c. The side view and top view of the inflated sample with the substrate of 35 μm -thickness PDMS film under ε_A of 0% to 95% are presented in Figure 4.9a-c. The performance under isotropic strain is also quite repeatable but when ε_A exceeds 75%, the sensor loses function (Figure 4.10d) and before that, the gauge factor, around 51.5, does not decrease as that under uniaxial strain does. As analyzed above, under uniaxial strain, normally, there are regular wrinkles in the film (Figure 4.11a), and the wrinkles structure under strain is critical for the crack propagation in the rigid film. However, the isotropic strain can apparently inhabit the wrinkle just like that shown in Figure 4.2b. It is hard to observe the wrinkle structure when applied isotropic strain, the crack becomes wider and the film even totally break in many places revealing the typical charging effect of PDMS under electron beam (Figure 4.11b-d). Thus, the resistance changing can still keep in the high level after the breaking of the thick ring region.

Figure 4.10 The durability and the surface morphology under isotropic strain. According to the mechanical simulation in c), sensors are fabricated in the strain concentration area as shown in b) and the top view a). The resistance changing with the isotropic strain is shown in d). Utilizing the high stretchability, the LED circuit still works when suffering sharp bending, 1D stretching and isotropic strain as shown in e). The signal driven by the rhyme “little star” is presented in f). The numbered musical notation is listed on top and below every peak induced by the note. Insets present the amplified two same melodies.

Figure 4.11 The durability and the surface morphology under isotropic strain. a) The resistance changing under different cyclic isotropic strain. b) The FESEM image of the sensor under uniaxial strain of 60%. c, d) The Low- and high- magnification of FESEM images of the sensor under isotropic strain of around 85%.

Based on the novel SSSs, a wide range of applications could be developed. When the resistance changing meets the requirement of the circuit, the SSSs can support it as the stretchable electrode. An LED and a “NTU” patterned SSSs are in series connection. When the power is on, whatever kind of strain is applied, the LED is always in lighting (Figure 4.10e). Furthermore, it is still a challenge to detect the small strain vibration such as below 1% by employing SSSs due to the low gauge factor. Herein, when the relatively small prestretch strain is applied, the intrinsic vibration frequency of PDMS film could be around 200 Hz that is similar with the normal sound. Thus, sound was used to induce small strains in the PDMS film. The sound employed here is from pitch C to high pitch one (Figure 4.10f) and the frequency is from 262 Hz to 523 Hz, the first three vibration

modes (Figure 4.12b) can estimate the strain concentration area and accordingly sensors were placed on. Nine basic pitches are recognized (Figure 4.13). Specially, it can be seen that many sub-wave modes are recorded (Inset of Figure 4.13a) indicating that the whole vibration damping process is captured which would be rather helpful.

Figure 4.13 The weak sound detection by using the novel sensor. a) The different pitches detected by the sensor. b) The displacement of the freestanding PDMS film under eigen vibrations. Accordingly, the sensor could be fabricated in the center covering certain area to detect different vibrations.

4.3.3 Long-term stability

The novel SSSs shows surprisingly good performance under uniaxial and isotropic strain which is quite vital for the practical application because the sensor will unavoidably suffer the multi-dimensional strain in practice. The strain rate of 10 mm/min was applied in order to eliminate the viscoelastic effect testing the intrinsic stretchability of the SSSs.

The thickness of the PDMS substrate is about 110 μm , and under the uniaxial tensile strain of 150%, it tends to break first, which determines the stretchability of the sensor (Figure 4.6a) and meanwhile indicates that the stretchability of thickness-gradient SWCNTs film is much higher than that of normally used stretchable gold film.⁸⁵ More importantly, the testing of the durability shows that the SSSs can suffer 60% strain of 100,000 cycles, 100% strain of 20,000 cycles where PDMS substrates tend to break, and still have rather stable performance (Figure 4.6b and Figure 4.7a). The original data at around 100,000 cycles under 60% strain and 20,000 strain under 100% is presented in Figure S5b and Figure 3c respectively. This durability is one of the best in reported SSSs, which hugely improves the service life taking a solid step towards the real application of SSSs. Besides, this novel SSSs still works in high temperature of up to 120 $^{\circ}\text{C}$ as shown in Figure 4.7c and due to the high thermal expansion coefficient of PDMS, the resistance response curve becomes lower but still keeps the changing characteristics which can be adjusted with certain calibration in practice.

4.4 Conclusions

In conclusion, through detailed investigation on the principle of stretchability of the rigid film on soft substrate, the mechanism of adjusting the gauge factor is developed. By constructing the film with gradient thickness, the seemingly contrary properties of brittleness and stretchability are combined together in one sensor endowing it with both high gauge factor and high stretchability. Based on this new strategy, novel thickness-gradient SSSs are fabricated with highly improved gauge factor, high durability and high uniaxial and isotropic stretchability based on the spinnig effect of the SWCNTs solution. This proposed novel strategy and fabricated high-performance stretchable strain sensors take a solid step towards the real application in various fields. The sound detection taking advantage of the highly improved gauge factor is demonstrated and the detailed damping vibration modes are recognized. Also, following the strategy, many other potential methods could be developed to improve the gauge factor of the sensor.

References:

- [1] D.-H. Kim, Ghaffari R., Lu N., Rogers J. A., *Annu. Rev. Biomed. Eng.* **2012**, *14*, 113-128.
- [2] S. Jung, Lee J., Hyeon T., Lee M., Kim D. H., *Adv. Mater.* **2014**, *26*, 6329-6334.
- [3] C. Yan, Kang W., Wang J., Cui M., Wang X., Foo C. Y., Chee K. J., Lee P. S., *ACS nano* **2013**, *8*, 316-322.
- [4] S. Xu, Zhang Y., Jia L., Mathewson K. E., Jang K.-I., Kim J., Fu H., Huang X., Chava P., Wang R., *Science* **2014**, *344*, 70-74.
- [5] N. T. Tien, Jeon S., Kim D. I., Trung T. Q., Jang M., Hwang B. U., Byun K. E., Bae J., Lee E., Tok J. B. H., *Adv. Mater.* **2014**, *26*, 796-804.
- [6] M. Melzer, Mönch J. I., Makarov D., Zabala Y., Cañón Bermúdez G. S., Karnaushenko D., Baunack S., Bahr F., Yan C., Kaltenbrunner M., *Adv. Mater.* **2014**.
- [7] D.-H. Kim, Lu N., Ma R., Kim Y.-S., Kim R.-H., Wang S., Wu J., Won S. M., Tao H., Islam A., *Science* **2011**, *333*, 838-843.
- [8] M. Ramuz, Tee B. C. K., Tok J. B. H., Bao Z., *Adv. Mater.* **2012**, *24*, 3223-3227.
- [9] A. Cirillo, Cirillo P., De Maria G., Natale C., Pirozzi S., *Sens. Actuators, A* **2014**, *212*, 110-122.
- [10] T. IláLee, SoonáJang W., SangáKim Y., LináWang Z., KooáBaik H., *Energ. Environ. Sci.* **2014**, *7*, 3994-3999.
- [11] J. Kim, Lee M., Shim H. J., Ghaffari R., Cho H. R., Son D., Jung Y. H., Soh M., Choi C., Jung S., *Nat. Commun.* **2014**, *5*.
- [12] H. S. Song, Kwon O. S., Lee S. H., Park S. J., Kim U.-K., Jang J., Park T. H., *Nano Lett.* **2012**, *13*, 172-178.
- [13] B. Zhu, Niu Z., Wang H., Leow W. R., Wang H., Li Y., Zheng L., Wei J., Huo F., Chen X., *Small* **2014**, *10*, 3625-3631.
- [14] A. P. Gerratt, Sommer N., Lacour S., Billard A. In *Stretchable capacitive tactile skin on humanoid robot fingers-first experiments and results*, Proceedings of the IEEE International Conference on Humanoid Robots, **2014**.
- [15] H. Nakamoto, Oida S., Ootaka H., Tada M., Hirata I., Kobayashi F., Kojima F. In *Application of stretchable strain sensor for pneumatic artificial muscle*, Robotic Intelligence In Informationally Structured Space (RiiSS), 2014 IEEE Symposium on,

IEEE: **2014**; pp 1-5.

[16] T. Yamada, Hayamizu Y., Yamamoto Y., Yomogida Y., Izadi-Najafabadi A., Futaba D. N., Hata K., *Nat. Nanotech.* **2011**, 6, 296-301.

[17] D. Son, Lee J., Qiao S., Ghaffari R., Kim J., Lee J. E., Song C., Kim S. J., Lee D. J., Jun S. W., *Nat. Nanotech.* **2014**, 9, 397-404.

[18] P. J. Mossop, McLachlan C. S., Amukotuwa S. A., Nixon I. K., *Nat. Clin. Pract. Cardiovasc. Med.* **2005**, 2, 316-321.

[19] D. Gamez, Fidjeland A. K., Lazdins E., *Bioinspir. Biomim.* **2012**, 7, 025008.

[20] D. J. Cohen, Mitra D., Peterson K., Maharbiz M. M., *Nano Lett.* **2012**, 12, 1821-1825.

[21] X. Wang, Li T., Adams J., Yang J., *J. Mater. Chem. A* **2013**, 1, 3580-3586.

[22] D. J. Lipomi, Vosgueritchian M., Tee B. C., Hellstrom S. L., Lee J. A., Fox C. H., Bao Z., *Nat. Nanotech.* **2011**, 6, 788-792.

[23] Y. Shang, He X., Li Y., Zhang L., Li Z., Ji C., Shi E., Li P., Zhu K., Peng Q., *Adv. Mater.* **2012**, 24, 2896-2900.

[24] L. Cai, Song L., Luan P., Zhang Q., Zhang N., Gao Q., Zhao D., Zhang X., Tu M., Yang F., *Sci. Rep.* **2013**, 3.

[25] J.-H. Kong, Jang N.-S., Kim S.-H., Kim J.-M., *Carbon* **2014**, 77, 199-207.

[26] M. K. Shin, Oh J., Lima M., Kozlov M. E., Kim S. J., Baughman R. H., *Adv. Mater.* **2010**, 22, 2663-2667.

[27] K. Liu, Sun Y., Liu P., Lin X., Fan S., Jiang K., *Adv. Funct. Mater.* **2011**, 21, 2721-2728.

[28] C. Pang, Lee G.-Y., Kim T.-i., Kim S. M., Kim H. N., Ahn S.-H., Suh K.-Y., *Nat. Mater.* **2012**, 11, 795-801.

[29] X. Xiao, Yuan L., Zhong J., Ding T., Liu Y., Cai Z., Rong Y., Han H., Zhou J., Wang Z. L., *Adv. Mater.* **2011**, 23, 5440-5444.

[30] F. Xu, Zhu Y., *Adv. Mater.* **2012**, 24, 5117-5122.

[31] S. Yao, Zhu Y., *Nanoscale* **2014**, 6, 2345-2352.

[32] F. Xu, Durham III J. W., Wiley B. J., Zhu Y., *ACS nano* **2011**, 5, 1556-1563.

[33] A. Chortos, Lim J., To J. W., Vosgueritchian M., Dusseault T. J., Kim T. H., Hwang S., Bao Z., *Adv. Mater.* **2014**, 26, 4253-4259.

[34] M. Park, Im J., Shin M., Min Y., Park J., Cho H., Park S., Shim M.-B., Jeon S., Chung

- D.-Y., *Nat. Nanotech.* **2012**, 7, 803-809.
- [35] S.-H. Bae, Lee Y., Sharma B. K., Lee H.-J., Kim J.-H., Ahn J.-H., *Carbon* **2013**, 51, 236-242.
- [36] Y. Wang, Yang R., Shi Z., Zhang L., Shi D., Wang E., Zhang G., *ACS nano* **2011**, 5, 3645-3650.
- [37] C. Yan, Wang J., Kang W., Cui M., Wang X., Foo C. Y., Chee K. J., Lee P. S., *Adv. Mater.* **2014**, 26, 2022-2027.
- [38] X. Li, Zhang R., Yu W., Wang K., Wei J., Wu D., Cao A., Li Z., Cheng Y., Zheng Q., *Sci. Rep.* **2012**, 2.
- [39] M. Hempel, Nezich D., Kong J., Hofmann M., *Nano Lett.* **2012**, 12, 5714-5718.
- [40] S. Cheng, Wu Z., *Adv. Funct. Mater.* **2011**, 21, 2282-2290.
- [41] N. Liu, Fang G., Wan J., Zhou H., Long H., Zhao X., *J. Mater. Chem.* **2011**, 21, 18962-18966.
- [42] B. Sun, Long Y.-Z., Liu S.-L., Huang Y.-Y., Ma J., Zhang H.-D., Shen G., Xu S., *Nanoscale* **2013**, 5, 7041-7045.
- [43] M. Kolloosche, Stoyanov H., Laflamme S., Kofod G., *J. Mater. Chem.* **2011**, 21, 8292-8294.
- [44] M. Li, Li H., Zhong W., Zhao Q., Wang D., *ACS Appl. Mat. Interfaces* **2014**, 6, 1313-1319.
- [45] J.-B. Chossat, Park Y.-L., Wood R. J., Duchaine V., *Sensors* **2013**, 13, 3405-3414.
- [46] J. Park, Wang S., Li M., Ahn C., Hyun J. K., Kim D. S., Kim D. K., Rogers J. A., Huang Y., Jeon S., *Nat. Commun.* **2012**, 3, 916.
- [47] J. T. Muth, Vogt D. M., Truby R. L., Mengüç Y., Kolesky D. B., Wood R. J., Lewis J. A., *Adv. Mater.* **2014**, 26, 6307-6312.
- [48] J. A. Rogers, Someya T., Huang Y., *Science* **2010**, 327, 1603-1607.
- [49] T. Yamada, Y. Hayamizu, Y. Yamamoto, Y. Yomogida, A. Izadi-Najafabadi, D. N. Futaba, K. Hata, *Nat. Nanotech.* 2011, 6, 296.
- [50] D. J. Lipomi, M. Vosgueritchian, B. C. Tee, S. L. Hellstrom, J. A. Lee, C. H. Fox, Z. Bao, *Nat. Nanotech.* 2011, 6, 788.
- [51] E. Roh, B. U. Hwang, D. Kim, B. Y. Kim, N. E. Lee, *ACS Nano* 2015, 9, 6252
- [52] S. Ryu, P. Lee, J. B. Chou, R. Xu, R. Zhao, A. J. Hart, S. G. Kim, *ACS Nano* 2015, 9, 5929.

- [53] R. Rahimi, M. Ochoa, W. Yu, B. Ziaie, *ACS Appl. Mat. Interfaces* 2015, 7, 4463.
- [54] X. Xiao, L. Yuan, J. Zhong, T. Ding, Y. Liu, Z. Cai, Y. Rong, H. Han, J. Zhou, Z. L. Wang, *Adv. Mater.* 2011, 23, 5440.
- [55] S. H. Bae, Y. Lee, B. K. Sharma, H. J. Lee, J. H. Kim, J. H. Ahn, *Carbon* 2013, 51, 236.
- [56] J. J. Park, W. J. Hyun, S. C. Mun, Y. T. Park, O. O. Park, *ACS Appl. Mat. Interfaces* 2015, 7, 6317.
- [57] J. B. Chossat, Y. L. Park, R. J. Wood, V. Duchaine, *IEEE. Sens. J.* 2013, 13, 3405.
- [58] H. Lee, B. Seong, H. Moon, D. Byun, *RSC Adv.* 2015, 5, 28379.
- [59] F. Xu, Y. Zhu, *Adv. Mater.* 2012, 24, 5117.
- [60] C. Pang, G. Y. Lee, T. I. Kim, S. M. Kim, H. N. Kim, S. H. Ahn, K. Y. Suh, *Nat. Mater.* 2012, 11, 795.
- [61] J. T. Muth, D. M. Vogt, R. L. Truby, Y. Mengüç, D. B. Kolesky, R. J. Wood, J. A. Lewis, *Adv. Mater.* 2014, 26, 6307.
- [62] J. A. Rogers, Someya T., Huang Y., *Science* **2010**, 327, 1603-1607.
- [63] S. P. Lacour, Chan D., Wagner S., Li T., Suo Z., *Appl. Phys. Lett.* **2006**, 88, 204103.
- [64] K.-Y. Chun, Oh Y., Rho J., Ahn J.-H., Kim Y.-J., Choi H. R., Baik S., *Nat. Nanotech.* **2010**, 5, 853-857.
- [65] Y. Kim, Zhu J., Yeom B., Di Prima M., Su X., Kim J.-G., Yoo S. J., Uher C., Kotov N. A., *Nature* **2013**, 500, 59-63.
- [66] Z. Liu, Yu M., Lv J., Li Y., Yu Z., *ACS Appl. Mat. Interfaces* **2014**, 6, 13487-13495.
- [67] L. Liu, Niu Z., Zhang L., Zhou W., Chen X., Xie S., *Adv. Mater.* **2014**, 26, 4855-4862.
- [68] Z. Huang, Hong W., Suo Z., *J. Mech. Phys. Solids.* **2005**, 53, 2101-2118.
- [69] Whitesides, G. M. & Grzybowski, B. Self-assembly at all scales. *Science* **295**, 2418-2421 (2002).
- [70] Chen, X., Rogach, A. L., Talapin, D. V., Fuchs, H. & Chi, L. Hierarchical luminescence patterning based on multiscaled self-assembly. *J Am Chem Soc* **128**, 9592-9593 (2006).
- [71] Xu, H. *et al.* Biomimetic antireflective hierarchical arrays. *Langmuir* **27**, 4963-4967 (2011).
- [72] Wong, T.-S., Chen, T.-H., Shen, X. & Ho, C.-M. Nanochromatography driven by

the coffee ring effect. *Anal Chem* **83**, 1871-1873 (2011).

[73] Zhang, Z. *et al.* Controlled Inkjetting of a Conductive Pattern of Silver Nanoparticles Based on the Coffee-Ring Effect. *Adv Mater* **25**, 6714-6718 (2013).

[74] Li, Q., Zhu, Y. T., Kinloch, I. A. & Windle, A. H. Self-organization of carbon nanotubes in evaporating droplets. *The Journal of Physical Chemistry B* **110**, 13926-13930 (2006).

[75] Zeng, H., Kristiansen, K., Wang, P., Bergli, J. & Israelachvili, J. Surface-induced patterns from evaporating droplets of aqueous carbon nanotube dispersions. *Langmuir* **27**, 7163-7167 (2011).

[76] Shimoni, A., Azoubel, S. & Magdassi, S. Inkjet printing of flexible high-performance carbon nanotube transparent conductive films by “coffee ring effect”. *Nanoscale* **6**, 11084-11089 (2014).

Chapter 5

Hair-mimicking soft sensors by 3D coffee ring effect*

Soft tactile hairs, which exist extensively on the animal and plant surfaces, have evolved into a unique self-amplified strain-sensing machinery and constitute a crucial soft mechanical sensing component capable of detecting subtle strains and interactions in the immediate environment without direct contact with the skin. The unique structure feature is that the sensing unit and strain reception are with stretchability and in 3D architecture and function differentiation, which poses a big challenge for bio-mimic fabrication. Here, to the knowledge for the first time, the 3D stretchable tactile electronic hairs (e-hairs) with isotropic stretchability was reported, which can detect multiple strains and the strain direction (any direction) with high sensitivity and stability by each single e-hair, and the unique underlying detection principle relies on the symmetry breaking of the resistance network at the root. Besides, the fabrication process is all-solution based by employing 3D printing and a capillary force-assisted self-pinning of carbon nanotubes. The e-hairs can be easily fabricated in an array format for efficient monitoring of gas and liquid flow.

*To be published substantially as Liu et al., Stretchable 3D-structured Multi-functional Tactile Electronic Hairs.

5.1 Introduction

Tactile hair constitutes a mechanical sensing machinery capable of detecting subtle strains and interactions in the immediate environment without direct contact with the skin.^[1-5] Most eukaryotic species, including spiders, bats, zebrafish and even the Venus flytrap, possess fine tactile hair capable of sensing minute forces and the orientation of air/water flow.^[6-8] For example, when someone bends or blows his/her sweat hairs, the tactile signal will immediately be transferred to the brain. The 3D architecture of the tactile hair renders it particularly effective for strain sensing. The body of the tactile hair acts as a stress amplifier that is transferring the external force acting on the tip to the root of the hair, where the sensing unit is safely protected beneath the skin. Also, the tactile hair possesses stretchability. One real hair, on the forearm for example, is capable of being lifted to as high as 5 mm with a peak force of ~ 0.2 N (Figure 5.1). This stretchability is vital for the real applications because the hair has to accommodate large deformations induced by the sudden pull/stretch forces.

Figure 5.1. Demonstration of the real tactile hairs. a, Images to present the stretchability of the tactile hair. b, Extension-force curve of a real tactile hair on the forearm of an adult Asian man.

Several previous studies reported electronic whiskers or cilia via composite materials to mimic the strain-detection function,^[9-11] however, it is still a big challenge to mimic the critical features and functions of tactile hairs including stretchability, multi-strain detection and strain-direction recognition by using single e-hair but not an e-hair-array.

Herein, a new strategy was proposed to fabricate 3D e-hairs composed of stretchable sensing units, rather than relatively rigid ones, by employing capillary force-assisted 3D self-pinning effect which is a cost-efficient all-solution based method and could be potentially achieved in a large scale through the booming printing technology. These e-hairs can still work under more than 120% tensile strain applied at the sensing unit and detect multiple strains and the corresponding strain direction by using one single e-hair with good stability (more than 10,000 strain cycles), which would offer an attractive avenue for the production of highly integrated and fast-responding strain-detection devices for stretchable electronics.^[12-26]

5.2 Experimental Methods

5.2.1 3D coffee effect of carbon nanotubes

After having established the optimal e-hair structure for strain detection, the next step would be to fabricate the structure for real-life application. The complex structure can be easily fabricated through 3D printing. However the deposition of a stretchable conducting film for strain measurement poses the major challenge. The stretchable conducting film must completely cover the out-of-plane gradient root region and part of the e-hair body to precisely monitor the strain concentration at the root. The most commonly available thin film fabrication methodologies (e.g., thermal evaporation and electro-deposition) are not suitable for a one-step deposition process on this complicated 3D structure. The previous study showed that single-wall carbon nanotubes (SWCNTs) modified with carboxyl could easily form the highly stretchable conductive film on flat PDMS substrate modified with hydroxy by utilizing self-pinning effect. Specifically, SWCNTs can be patterned in any shape and not only form outer rings as normally done by simple self-pinning effect, but also fully cover the whole substrate with CNT film, which is essential for both high stretchability and high sensitivity. In-plane self-pinning effect has been investigated extensively from the mechanism behind to the mathematical model²⁹⁻³². However, few studies were on the self-pinning effect in out-of-plane direction that would help to construct 3D macroscopical structure with nanomaterials.

To address it, the capillary force-mediated self-pinning effect of single-wall carbon nanotubes (SWCNTs) was further developed in the out-of-plane direction. Specifically,

after construction of the optimal e-hair structure through 3D printing, the SWCNTs solution is dropped at the e-hair root and allowed to climb the hair body (height of around 2 mm) through capillary action during which the self-pinning effect enables the formation of out-of-plane SWCNTs film. The unique feature of the method is that SWCNTs cannot only form ring structure on the outside, but also fully cover the region inbetween the rings with a thin film. The method is also suitable for deposition even on thin e-hair of diameter $\sim 25 \mu\text{m}$. It can be observed that multiple rings are formed on the e-hair body, which would facilitate the detection of strain distribution throughout the e-hair. Two major non-coplanar ring regions also can be observed; one at the bottom of the e-hair root and another on the body, which can be used as connection points in the following encapsulation and testing process.

5.2.2 Electrical and mechanical testing

Under current five-point encapsulation method, if the direction of applied strain is on neither BC nor DE, but slopes at certain angle with them, how to identify the direction? Obviously, R_{AB} and R_{AE} are in the compressed region under this situation and tensile region for R_{AC} and R_{AD} . The performance of R_{AB} , R_{AC} , R_{AD} and R_{AE} under this situation were checked, finding that both R_{AB} and R_{AE} decrease at bending angle of 15° , and both R_{AC} and R_{AD} increase at the same time. Therefore, the sloping direction can also be roughly identified by using this five-point method. And following the proposed strategy, the direction could be more precisely recognized by increasing the connecting points on the lower ring.

Moreover, R_{AB} is highly sensitive to the bending angle. Here, the sensitivity, i.e., the gauge factor (GF), so GF achieves to about $24\% \text{ deg}^{-1}$, i.e., when it has only 1 bending degree changing, R_{AB} will increase by 24%. The e-hair, with this high sensitivity, can detect the pressure driven by the soft wind and water flow as demonstrated later. The stability for the bending process is also tested and it shows repeatable performance of R_{AB} and R_{AC} even after 1,000 bending cycles at bending angle of 15° . Details could be referred to following contents (Figure 5.8 and 5.10).

5.3 Principal Outcomes

5.3.1 Stable hair-like sensor fabricated

Herein, the concept of stretchable strain-sensing electronic hair was proposed and a new strategy to demonstrate it by employing capillary force-assisted three-dimensional (3D) self-pinning effect was introduced which is a cost-efficient all-solution based method and could be potentially achieved in a large scale through the booming printing technology. The proposed concept will open up for exploration of stretchable hair-like sensors for e-skin, smart robots and other soft electronics. The new strategy introduced involves a series of delicate designs which collaborate closely to achieve the desire sensing property. The structure of the stretchable strain-sensing hair is mechanically optimized firstly achieving the efficient strain transferring from the top to the bottom. The new phenomenon of jumping self-pinning process in the vertical direction under the help of capillary force is observed making multiple parallel rings on the hair, through which the strain on the hair can be detected segmentally. Most importantly, the direction of applying strain can be distinguished by corporately utilizing the rings on the hair and that at the bottom. Also, the related principle, i.e., the symmetry breaking of the resistance network, is fully investigated. The stretchable strain-sensing hair can detect multiple strains, including tensile, compressed, and bending strains possessing high sensitivity, as high as 0.18 per deg; high stability, withstanding more than 1000 cycles. Also, it was demonstrated that it can be fabricated in array and efficiently detect the airflow and water flow.

The sensing part would be fabricated on the bottom of e-hair, just like the real hair, in order to protect sensing unit from scratch/friction. Therefore, the e-hair structure must benefit the strain transferring from the hair body to the root, especially for bending strain, i.e., the peak strain, and the area of strain concentration, in the root should be maximized, which helps to keep good sensitivity. It requires that the structure of e-hair be carefully designed. Ideally, the strain energy could be totally transferred from the top to the root where the sensing unit is located.

Figure 5.2 Bio-inspired stretchable tactile electronic hairs and structural mechanical optimization. **a**, Diagram of the response of tactile hairs to mechanical stimuli, and the stretchable tactile electronic hairs inspired by this process. **b**, Three-step mechanical optimization based on energy conservation and classical bending moment theory, and four structures (I, II, III, IV) developed correspondingly. The final optimized structure (IV) comprises two parts: a hair body with a stiffener of polylactic acid (PLA) and a hollow root. **c**, The strain concentration and distribution under the bending angle of 45° as calculated by FEM simulation for the four different structures proposed in (b). The negative value reflects compression. **d**, Strain concentration in the four different structures in (a) under different bending angles. **e**, Strain distribution areas in the four structures in (a) under the bending angle of 45°.

Here, the design routine of structural mechanics starting from the most basic one was followed. One simple model of the e-hair could be the type of directly inserting the soft hair into the elastic substrate (Type I, Figure 5.2b). For this situation, the whole substrate is the strain buffer zone that can assist in absorbing the strain energy, and the strain is hard to be concentrated at the root inducing the sharp decrease of both ϵ and σ in the root as suggested by finite element modeling (FEM) (Figure 5.2c-e). Specifically, strain concentration is much smaller for both tensile and compression strain (Figure 5.2e), indicating that the sensitivity of the e-hair would be lower. Thus, first of all, the overall distribution volume of strain was tuned by constructing a gradient transition region between the hair and the elastic substrate (Type II, Figure 5.2b). It would benefit the patterning of the sensing material in terms of avoiding the sharp transition and take the responsibility of consuming applied strain energy instead of the whole substrate, so the strain distribution would be mainly in this area. Further, according to the classical formula of strain energy, the relationship between the external work, W , and the inner deformation energy could be constructed as follows: $W = \frac{1}{2} E \int_V \epsilon^2 dV$, where E is the Young's modulus, ϵ is the strain induced, and V is the volume. According to the mean-value theorem of integrals, it could be always described as $W = \frac{1}{2} E \bar{\epsilon}^2 V = \frac{1}{2} E \bar{\epsilon}^2 A_e \bar{h}$ where $\bar{\epsilon}$ is the mid-value, and $\bar{h}$ is the average thickness. Thus, for a given external work applied, could be maximized by relatively reducing the volume, e.g., by hollowing this gradient transition region (Type III, Figure 5.2b). The FEM shows that A_e increases dramatically from Type I to Type III (Figure 5.2e), however, ϵ_c just slightly increases (Figure 5.2d) which is mainly ascribed to the softness of the hair itself and large area of strain distribution can be observed on it (Figure 5.2c,d). Again, the classical theory of bending moment was used. The e-hair could be simplified as an ideal beam, and the formula of the force in the root should be as: $F = 3EIy/L^3$, where y is the deflection, E is the Young's modulus, L is the length of the e-hair, and I is the inertia moment. Thus, $F \sim 3EIy_{max}/L^3$ and then, for a specific e-hair with a given length and applied with a certain y_{max} , ϵ_c is decided by the stiffness, EI . So, how to enhance the stiffness of the e-hair is a critical issue. The design of coaxial composite e-hair is adopted to overcome it and Young's modulus of the core, which is much larger than that of the surrounding soft

polymer (Polydimethylsiloxane), is utilized to increase its stiffness enhancing the ability of strain transferring. The FEM proves that k is increased significantly (Figure 5.2d), and is hugely enlarged both for tensile and compression strain (Figure 5.2d and see top view in Figure 5.3a) after this four-step optimization. So far the design has been ready to be used to demonstrate the proposed concept. It should be emphasized that there could be further optimization following this routine, e.g., by adjusting the shape parameter of the conic root and modulus of the polymer and the stiffener.

Figure 5.3 FEM simulation for strain distribution of different e-hair structures. a-c, the topview and sideview of the e-hair with full substrate, hollow substrate, and hollow substrate with stiffener inside the hair body, respectively.

For the structure design of the e-hair, the out-of-plane gradient root is vital for enhancing the sensitivity of the sensor unit (Figure 5.2c). However, how to make the sensor film fully cover on it and partially on the e-hair, in order to precisely monitor the strain concentration at the root (Figure 5.2c), by using a facile method is a big challenge,

because most of the film fabrication method, e.g., thermal evaporation, electrodeposition, cannot realize one-time forming on this complicated 3D structure. Nevertheless, self-pinning effect, as a unique self-assembling process, provides an extremely efficient way to pattern and functionalize nanomaterials in relatively large scale by utilizing the non-equilibrium mass-transfer process during the solution evaporation, and may help to successfully deposit active materials on 3D substrates due to the wetting process.

The previous study showed that single-wall carbon nanotubes (SWCNTs) modified with carboxyl could easily form thickness-gradient carbon nanotube films with the stretchability of more than 150% on flat PDMS substrate modified with hydroxy by utilizing self-pinning effect. Specifically, SWCNTs can be patterned in any shape and not only form outer rings as normally done by simple self-pinning effect, but also fully cover the whole substrate with CNT film of different thickness, which is essential for high gauge-factor sensor. In-plane self-pinning effect has been investigated extensively from the mechanism behind to the mathematical model. However, few studies were on the self-pinning effect in out-of-plane direction that would help to construct 3D macroscopical structure with nanomaterials.

Figure 5.4 On-hair multiple rings and the corresponding application to detect on-hair strain distribution. a, Image of typical on-hair five rings. b, Surface profile data of the five rings in (a). c, The velocity and displacement monitored by high-speed camera. Red and green segments are to illustrate the velocity jumping and dropping. d, This multiple rings can be employed to test

the detailed deformation on the hair by careful encapsulation.

Herein, combining with the gradient transition root of the e-hair, it is found that the capillary force would help to overcome the gravity of the solution, which drives the self-pinning effect in the out-of-plane direction. Following the previous structure design, firstly, we 3D printed the template with the desired shape and the hair part on the template would be taken as the stiffener stick inside the e-hair subsequently. Then the PDMS film was coated on it. After curing, the film was peeled off with the stiffener stick inside, and then was locally hydrophilic by employing proper oxygen plasma. Finally, SWCNTs solution was dropped on and would immediately cover the whole gradient root including part of the hair under the help of capillary force. After the evaporation of around thirty minutes, the SWCNTs rings and film were successfully deposited on the root. During this process, surprisingly, a new physical phenomenon was observed by closely checking the evaporation process on the hair. It was found that there were multiple rings, proved by the thickness profile data, on the hair after the evaporation, indicating that the pinning process is not continuous but more like a jumping one. To fully understand the mechanism behind, the evaporation process was monitored by using a high-speed camera and tracked the dropping of liquid level on the hair. The jumping phenomenon of the liquid level was clearly revealed. Its displacement was analyzed by image post processing (Figure 5.4). Sudden increases in its displacement can be observed and there was velocity peaks correspondingly. The formation of multiple rings on a flat substrate has been observed by carefully controlling the solute and evaporation conditions. However, few reports were on the multi-ring formation in the out-of-plane direction, which would play a key role in the detection of strain direction and detailed strain distribution on the hair in the following investigation. The principle behind it should be similar to that in the flat substrate, because only gravity is introduced into the dynamic system and the governing mechanism, which is the balance among the pinning force, capillary force and gravity, does not change. Also, there is the gradient thickness of the multiple rings on the vertical hair as that on the flat substrate has. Those multiple rings could be also utilized to monitor the strain changing on the hair by taking the adjacent rings as the connecting points and testing the resistance vibration. Further, following this strategy, multiple rings were also induced on the flat substrate without any external assistance and subtle evaporation controlling, only through introducing the vertical

boundary by folding the flat film, which indicates that what it has been found could be further explored to achieve multi-ring effect opening up for new method of nano-materials patterning.

5.3.2 Full stretchability of this sensor

Figure 5.5 Soft tactile electronic hairs with out-of-plane multiple rings by the 3D self-pinning effect and their performance with respect to strain sensing. a, Diagram of the slip-and-stick self-pinning effect which is essential for the formation of the out-of-plane multiple rings and CNT thin film on the e-hairs. b, Image of a fabricated e-hair. Inset illustrates the five-point encapsulation method. c, Optical images of the e-hair during stretch and the corresponding strain distribution by FEM method shown in d. e, Resistance change with different strain concentration applied to the sensing unit. Normalized resistance, R/R_0 , where R and R_0 are the resistance values monitored with and without applied strain. The inset shows how the strain is applied. f, The

durability of the e-hair under tensile strain. Tensile strain of 120% at the sensing unit was applied for over 10,000 strain cycles.

The fabricated e-hair is presented in Figure 5.5a,b. There are two non-coplanar ring regions: one is at the bottom and another at the top, which will be used as the connecting part in the following encapsulation and testing process (inset of Figure 5.5b). As investigated before, the in-plane SWCNTs film possesses full stretchability, but the stretchability of the out-of-plane one suffering the out-of-plane strain has to be studied first, because the real hair is relatively stretchable and the fabricated sensor unit should possess stretchability to work for e-skin. The sample was attached firmly on a rigid substrate, and then was applied with tensile strain in the vertical direction (inset of Figure 5.5c). The strain applied is defined according to the original length of the hair part (around 15 mm). Thus, 30% strain, i.e., the extension of 4.5 mm, is comparable to the limit of the real hair. E-hair presents high stretchability during the test, even after 1000 strain cycles at 30% strain (Figure 5.5d), indicating that the out-of-plane SWCNTs film keeps its stretchability and stability. It also shows good performance under the compression strain (Figure 5.5). Those good stretchability and stability provides a basic platform for the strain-sensing function of the e-hair, especially for the bending strain, a typical strain that the hair normally suffers. Besides, this effect is also applied to the fine hair with smaller diameter (Figure 5.6). After the successful fabrication, the performance of the hollowed hair is compared with that with full substrate to verify the hypothesis proposed previously (Figure 5.7). The diameter of the e-hair is tunable, and an e-hair with diameter of only around 25 μm was demonstrate here (Figure 5.7a). It also possesses the structure of gradient roof (Figure 5.7b) and the similar surface morphology when being bended (Figure 5.7c). It indicates that e-hairs could be fabricated in relatively small diameter increasing the integration level and spatial resolution of the sensing function.

Figure 5.6 E-hair fabricated with diameter of around 25 μm . a, Image of the fine e-hair. b, FESEM image of the gradient root. c, Typical cracks and wrinkles structure on the root.

Figure 5.7 Comparison of relative resistance change between the structure with hollow root and the full root. Result shows that the resistance changes more significantly in hollow root than that in full root, indicating that the strain transferring is more efficient in hollow one

5.3.3 Strain direction recognition

For the bending strain, it is highly desirable for the e-hair to distinguish the direction of the strain applied, which would open up for exploration of delicate strain tracking. According to the previous FEM simulation, it is obvious that the strain distribution in the root could be roughly divided into four regions: tensile region (i), compressed region (iii), and two side regions (ii, iv). Thus, the direction can be recognized theoretically as long as Region i and Region iii are figured out. Since the ring on the hair is just located in the parting between Region i and Region iii, it would play a vital role in reflecting the strain distribution by monitoring the resistance vibration. Therefore, during the encapsulation, i.e., the wire bonding and testing process, the ring on the hair would be a critical connecting point. Specifically, five wire bonding points were chosen: one is on the hair (Point A) and the other four are on the four principal directions (Points B-E), and monitor the resistance between Point A and the other four. When the bending strain is applied in one direction, e.g., from point B to point C, R_{AB} , R_{AC} , R_{AD} and R_{AE} , where R is the

resistance between related points, are measured individually (Figure 5.8). It is observed that R_{AB} , always larger than the initial value, increases with the bending angle, however, R_{AC} decreases at the beginning and then almost keeps constant afterwards, and R_{AD} , R_{AE} nearly do not show any changing with the increase of the bending angle. This diverse changing feature is critical for distinguishing the strain direction. The rising of R_{AB} is definitely ascribed to that the shortest electron path from Point A to Point B is suffering stretching strain, and the decreasing of R_{AC} is due to the compression (Region i and iii, Supplementary Fig. 1a). R_{AB} is highly sensitive to the bending angle. The e-hair, with this high sensitivity, can detect the pressure driven by the soft wind and water flow as demonstrated later. Besides, the reason why R_{AC} decreases first and then nearly keeps constant is that the compression can only connect the cracks in the CNT film initially but cannot contribute further increase in the resistance.

For stretchable e-hairs, except the direction recognition, their performance under isotropic strain is also of importance for real applications, since they would inevitably suffer the multidimensional strain in practice even when they are supposed to be applied one-dimension tensile strain. On the other hand, the isotropic stretchability is difficult to be achieved requiring more complicated design. The previous study has shown that the CNT film formed by self-pinning effect on the 2D flat substrate possesses isotropic stretchability. Herein, the isotropic stretchability of e-hairs fabricated by 3D self-pinning effect is checked. Firstly, the e-hair array is successfully fabricated indicating that it can be utilized in a large scale, and the booming printing technology could be employed to make a facile and rapid fabrication process, since the self-pinning effect is a solution based method. Then, the two edges of the array are fixed on a hollowed rigid substrate (Figure 5.9) and a stick with lubricant on its head and larger diameter than that of sub-hollowed roof in the e-hair applies vertical stress from the bottom (Figure 5.9). It shows that the changing trend of the resistance in different strain domain still keeps the same with that without isotropic strain applied. The resistance changing in compression side is more significant which is ascribed to bridging cracks induced by the pre-isotropic strain. This result proves that the e-hair possesses isotropic stretchability and can keep its performance under isotropic strain. Moreover, the e-hair array can be fully used to recognize the tactile pattern, e.g., a tactile path with 'NTU' shape (Figure 5.9). This ability of pattern recognizing will be of importance for the e-skin and smart robots

endowing them with the ability to sense the external complex stimuli, in which it is no need to touch directly on the sensor system.

Figure 5.8 The resistance network modeling based on the strain distribution and related surface morphology under bending strain. a, Normalized resistance with different bending angle in different strain regions (see Supplementary Fig. 1a). b, The durability of the e-hair under bending strain. The inset presents the diagram of tensile strain and compression strain regions with black color and pink color respectively. c-d, Cracks and wrinkles distribution in tensile region (Region i) and compressed region (Region iii) under the bending angle of 60° , respectively. e, The resistance network is abstracted through three-step modeling. The four regions correspond to that analyzed in Supplementary Fig. 2 and the four resistors in the final model.

Figure 5.9 Isotropic stretchability of the e-hair array. Images to present how the isotropic strain is applied in practice with smaller strain in (a) and larger strain in (b). c, The e-hair array could be used to identify the touching pattern, like a ‘NTU’ pattern

Under current five-point encapsulation method, if the direction of applied strain is neither on BC nor DE, but slopes at certain angle with them (Figure 5.10), how to identify the direction? Obviously, R_{AB} and R_{AE} are in the compressed region under this situation and tensile region for R_{AC} and R_{AD} . the performance of R_{AB} , R_{AC} , R_{AD} and R_{AE} under this situation were checked, finding that both R_{AB} and R_{AE} decrease at bending angle of 15 deg., and both R_{AC} and R_{AD} increase at the same time (Figure 5.10). Therefore, the sloping direction can also be roughly identified by using this five-point method. And following the proposed strategy, the direction could be more precisely recognized by increasing the connecting points on the lower ring.

Figure 5.10 Direction recognition when the direction of the bending strain slopes to that of encapsulation wires. a, Diagram to illustrate this situation under five-points encapsulation method. b-e, The resistance changing testing from point A to corresponding points, respectively.

Figure 5.11 FESEM images of the e-hair under bending strain. a, Image to present the boundary (red dash line) between the region iii and region iv as shown in Figure 3a. b, The on-hair multiple rings (between red dash lines) under the bending strain. The hair body is rotated to make it in horizontal under the FESEM. c, The lower ring on the root (between the red dash lines). Inset illustrates the typical magnified view of an area beside the lower ring on the root.

For better understanding the behavior of resistance changing and generalizing the strategy, the structure of the SWCNT film when suffering bending and the related physical model

behind should be fully investigated. According to the FEM analysis (Figure 5.11), the film can be roughly divided into four regions (i-iv) (top view in Fig. 4a) corresponding to related strain state (Figure 5.11). Herein, the e-hair under bending strain was further observe by employing the field emission scanning electron microscopy (FESEM), showing that the surface morphology of the film in the four regions is totally different and the boundary of the regions induced by the different strain domain, e.g., between Region iii and iv, can be distinguished clearly (Figure 5.11). Specifically, the crack is orthogonal to the stretching direction in Region i and parallel to the compression direction in Region iii. In contrary, the induced wrinkle is parallel to the stretching direction in Region i and orthogonal to the compression direction in Region iii. The crack blocks the conducting path in Region i increasing the resistance, but is parallel to that in Region iii which has little effect on the resistance. However, wrinkles in Region iii will shorten the conducting path to some extent resulting in the decrease of the resistance. All of those predicted performance of resistance has previously been proved by the experimental data (Figure 5.12).

Figure 5.12 Results of resistance network modeling and related experimental data for reference. a, Resistance changing predicted by the resistance network model in Figure 3e. b, Experimental data of the resistance vibration from point B to point C.

Further, the ring part is also examined carefully, since all the connecting points of wire bonding are on the ring during the resistance testing process. It is found that there is typical gradient thickness from the on-hair ring part to the on-hair inner thin part which is verified by the gradient wavelength (Figure 5.13) according to the buckling theory. This gradient thickness was also found for self-pinning effect on 2D flat substrate in the

previous study, indicating that the 3D self-pinning effect could still follow the same film-forming mechanism with that on 2D flat substrate during the pinning process. Besides, the detailed observation for the thick ring part reveals that there is no throughout cracks in it, because no strain is applied along the ring itself during the bending process, therefore, it is ideal for the wire bonding by taking the connecting points on this ring part. This analysis is also applicable to the lower ring.

Figure 5.13 Gradient wavelength from the thick on-hair ring part (region ①), transitional part (region ②) to inner thin part (region ③). a, On-hair thickness-gradient SWCNTs film. The e-hair is rotated to make the on-hair ring in horizontal under FESEM. The on-hair film can be roughly divided into three regions: thick ring part (①), transitional part (②) and inner thin part (③), according to the wavelength of the wrinkle corresponding to the thickness of the film. b, The detailed observation of the thick ring part in (a) and the definition of the wavelength. c, Wavelength changing in different regions.

Based on those analyses, the resistance model can be built up as illustrate in Figure 5.8e. Since there is only one connecting point on the on-hair ring, it is equivalent to an equipotential node. And the lower ring is divided into four parts by the four connecting points. The four strain domains turn to be four resistors accordingly. By applying the classical Kirchhoff's law, the formula is $\sum_i I_i = 0, \sum_k V_k = 0$, where i is i_{th} node, k is the k_{th} circuit, I is the current and V is the voltage. The equivalent resistance between every two nodes could be calculated. Thus, the strain applied can be simulated by increasing or decreasing R_n ($n = i, ii, iii$ and iv) according to the different strain domain. Due to the symmetry of this circuit, the resistance of R_i and R_{iii} can be tuned, and calculate the equivalent resistance of R_{AB} and R_{BC} to investigate whether the experimental data can be explained (Figure 5.8e) and prove that it is the breaking of the circuit symmetry that

helps to distinguish the direction of strain applied. When the bending strain is applied from B to C and from C to B, R_{BC} does not change at all due to the symmetry of this circuit which is also proved by the experimental data (Figure 5.12a), however, R_{AB} changes significantly with different strain domain (Figure 5.12b). Therefore, if there is no Node A that could be utilized to test the resistance, the direction information would be lost, indicating that the on-hair ring is vital for breaking the symmetry of the circuit and distinguishing the direction of strain applied.

5.3.4 Air and water blow detection

Figure 5.14 Isotropic stretchability of the e-hair array and detection of subtle fluid flow. a, Photograph of the e-hair array. b, The normalized resistance change under different speeds ranging from 1 m/s ~ 11 m/s. c, The stability of the detection signals under the nitrogen speed of 5.7 m/s. d, The amplified view reveals that the damping vibration dominates the later part of the signal as illustrated in the inset. e, Signal obtained under different water speeds corresponding to two different flow states: laminar flow and turbulence flow. The green square indicates a typical signal of laminar flow and the inset shows the magnified view. The red ellipse highlights the typical vibration signal of the e-hair driven by the turbulence flow. The red rectangle shows

the signal induced by the sudden shut-off of the water flow.

Figure 5.15 Resistance response for different applied gas speed of nitrogen: 3.3 m/s in (a) and 1 m/s in (b).

As introduced before, in nature, bats and Zebrafish make use of the hairy sensory system to sense the airflow and water flow assisting flying in the sky and swimming under the water, respectively. Inspired by this, the e-hair can also detect the gas and water flow with high sensitivity. In order to further enhance the sensitivity to the gas flow, a small fan-shaped modification on the hair structure is added to receive the gas force more efficiently, and then different speed of nitrogen flow is applied to the e-hair. The resistance of tensile strain domain is monitored to sense the nitrogen flow from the speed of 1 m/s to around 10.5 m/s occupying five speed regions from light flow to fresh breeze (Figure 5.14a,b) according to the standard windspeed classification. Light flow (0.3-1.5 m/s) is the weakest wind speed region in which wind motion starts to be visible in smoke. It can induce around 20% changing in resistance, and arouse increase by a factor of about 10 for the region of fresh breeze (8.0-10.7 m/s) (Figure 5.14c,d). More excitingly, the damped vibration of the e-hair after receiving a pulsed gas pressure for both low and high wind speed can also be monitored (Figure 5.15), which could be an important information for the vibration recognition. In sum, the e-hair can sense both weak and strong gas flow with the significant discrimination and could be extensively utilized in the field of flying control and wind field analysis. As for water flow detection, it is hard to observe the

damped signal because the viscosity of water is much larger than that of nitrogen and the balance between the water pressure on the hair and the strain induced in the root can be built in a static manner but not through vibration. Therefore, it can be found that the resistance increasing is not as sharp as that under nitrogen pressure and it will decrease to some extent but not back to original state reflecting the balance building process. Moreover, the e-hair still can record the signal induced by different speed of water flow. And when the speed increases to around 1 m/s in a rubber tube with diameter of 5 mm (Reynolds number is about 5000), the flow state turns to be of turbulence which is a typical transformation in fluid, which can also be reflected in the signal monitored (Figure 5.14e). It indicates that the e-hair could be utilized to distinguish the fluid speed and state transformation which is critical for fluid flow sensing. More specifically, once the switching of input water is suddenly shut off, there will be vibration wave inside the water induced by the fluid inertia, which can also be recognized by the e-hair. This ability to sense the fluid flow could benefit the fluid field analysis, under-water robot and microfluidic control.

5.4 Conclusions

Always taken as the small affixture on skin, stretchable hair-sensing system, however, possesses multi-functional sensing ability and could sense tension, compression and bending, providing the basic function of sensing airflow, water flow and other subtle touch that does not directly contact with skin. In order to mimic those functions, it requires a systematic design to make the e-hair possess high sensitivity, isotropic stretchability and meanwhile, achieve the delicate integration of the structure optimization and the active material fabrication.

Analysis of structural mechanics is the first critical step to design the structure of the e-hair by considering the efficient strain transferring from the hair body to the sensing unit below. This design should maximum the strain concentration and its covering area in the root achieving high sensitivity. The simplest structure was studied and the desired gradient hollowed root with stiffener inside the hair after four-step optimization was obtained under the help of FEM simulation. And then since the desired structure is the out-of-plane one with 3D spatial configuration but not the conventional 2D flat one, how

to integrate it with active materials is a challenge.

A new strategy was proposed, capillary force-assisted 3D self-pinning effect, utilizing the advantage of both the climbing provided by the capillary force and self-assembling process of the self-pinning effect. This seamless integration meets all the above requirements of the e-hair even including the ability to distinguish the direction of the strain applied which is critical for many applications. The mechanism behind this ability is proposed and the key point is to break the symmetry of the resistance networks under the assistance of multiple out-of-plane rings supported by the new strategy. Also, many other schemes could be carried out following this proposed mechanism by employing other active materials to achieve the direction recognition of the strain applied. Like the real hair, the e-hair can be easily integrated in a large scale and used to detect multiple strains, very soft gas flow and fluid flow. Plenty of flow details can be monitored including flow speed, damping vibration, quasi-static force balance and flow state. Additionally, it has to be emphasized that the 3D printing technology and solution-based active material process are employed here which make the whole process cost-efficient and high-yielding even for a large scale. The concept of stretchable e-hair and related design principles proposed open up for exploration of new sensing unit for the artificial skin, smart under-water robot and flow field analysis making a solid step towards the interactive sensing and adaptable interfaces. .

References:

- [1] Tobin D. J. *Chem. Soc. Rev.* **35**, 52-67 (2006).
- [2] Tobin D. J., Kauser S. *Mol. Cell. Endocrinol.* **243**, 1-11 (2005).
- [3] Bleckmann H., Joachim M., Coombs S. L. *Flow sensing in air and water* (Springer Press, 2014).
- [4] Beem H. R., Triantafyllou M. S. *arXiv:1501.04582* (2015).
- [5] Volkov A. G., Carrell H., Markin V. S. *Plant Physiol.* **149**, 1661-1667 (2009).
- [6] Barth F. G., Humphrey J. A., Secomb T. W. *Sensors and sensing in biology and engineering* (Springer Press, 2012).

- [7] Monteiro-Riviere N. A. *Toxicology of the Skin Ch.1* (CRC Press, 2010).
- [8] Halata Z. *J. Invest. Dermatol.* **101**, 75S-81S (1993).
- [9] Takei K. *et al. Proc. Natl. Acad. Sci.* **111**, 1703-1707 (2014).
- [10] Harada S., Honda W., Arie T., Akita S., Takei K. *ACS Nano* **8**, 3921-3927 (2014).
- [11] Alfadhel A., Kosel J. *Adv. Mater.* **27**, 7888-7892 (2015).
- [12] Tee B., Wang C., Allen R., Bao Z. *Nature Nanotech.* **7**, 825-832 (2012).
- [13] Zhu B. *et al. Adv. Mater.* **28**, 1559-1566 (2016).
- [14] Boland J. J. *Nature Mater.* **9**, 790-792 (2010).
- [15] Rus D., Tolley M. T. *Nature* **521**, 467-475 (2015).
- [16] White T. J., Broer D. J. *Nature Mater.* **14**, 1087-1098 (2015).
- [17] McEvoy M. A., Correll N. *Science* **347**, 70-74 (2015).
- [18] Wang H. *et al. Adv. Funct. Mater.* **25**, 3825-2831 (2015).
- [19] Sekitani T. *et al. Nature Mater.* **8**, 494-499 (2009).
- [20] Wegst U. G. K., Bai H., Saiz E., Tomsia A. P., Ritchie R. O. *Nature Mater.* **14**, 23-36 (2015).
- [21] Zhu B. *et al. Small* **10**, 3625-3631 (2014).
- [22] Lee H. *et al. Nature Nanotech.* doi: 10.1038/nnano.2016.382016 (2016).
- [23] Liang J. *et al. Nature Commun.* **6**, 7647 (2015).
- [24] Wang X., Gu Y., Xiong Z., Cui Z., Zhang T. *Adv. Mater.* **26**, 1309-1309 (2014).
- [25] Zarek, M., Layani, M., Cooperstein, I., Sachyani, E., Cohn, D. and Magdassi, S. *Adv. Mater.* doi: 10.1002/adma.201503132 (2016).
- [26] Zang, Y., Zhang, F., Huang, D., Di, C.-a. and Zhu, D., *Adv. Mater.* **27**, 7979–7985 (2015).

Chapter 6

Structured fibers for fiber-shaped stretchable strain sensors*

Stretchable strain sensors are critical components for wearable electronics to obtain the real-time mechanical feedback for applications in healthcare, rehabilitation, human power enhancement and so forth. In this work, a new fiber-shaped stretchable strain sensor is reported. The vision of improving the sensitivity of the stretchable strain sensor could be shifted from the active materials engineering to the mechanical design of the elastic substrate. A novel strategy that enables surface strain redistribution in elastic substrate to significantly enhance the sensitivity is introduced. Such enhancement method attributes to the delicate structure of beads on a fiber based on the principle of Plateau-Rayleigh instability. Also, a new method of transient thermal curing is proposed for large-scale fabrication of PDMS fibers with predefined diameter.

*To be published substantially as Liu et al., Surface Strain Redistribution by Structured Fibers for High-performance Fiber-shaped Stretchable Strain Sensors.

6.1 Introduction

Stretchable strain sensors, as one of the critical components in wearable electronics, are under fast development driven by recent advances in integrating electronic components with humans to obtain the real-time mechanical feedback for applications in healthcare, rehabilitation, human power enhancement and so forth.^[1-6] Fiber-shaped stretchable strain sensors with small testing areas possess huge potential in being directly weaved into textiles. Such sensors are becoming more accessible in terms of wearability and integrability, making fiber-shaped sensors an increasingly important research field.^[7-16] Recently, non-fiber-shaped stretchable strain sensors with flat structures have been extensively developed including sensors based on graphene/graphene oxide, carbon nanotubes, liquid metals, metal-semiconductor hybrids, hydrogels, self-healing materials, conducting polymers and micro fluidics.^[17-47] In comparison, fiber-shaped stretchable strain sensors have been less explored.^[14, 48-53] The sensitivity achieved is still far away from satisfactory and the enhancement method is rarely addressed. The reasons behind are as follows. First of all, compared to mature technologies like spin coating, that enables fabrication of homogeneous flat films with desired thickness, it is still a big challenge to produce stretchable micro fibers with controllable diameters at large scale using established thermosetting polymers like polydimethylsiloxane (PDMS). Secondly, compared to well-established photolithography techniques that have been extensively applied to fabricate nano/micro patterns on flat geometries, it is quite difficult to introduce such structures on a single fiber.

Herein, a new fiber-shaped stretchable strain sensor is reported. An innovative process is introduced that enables surface strain redistribution in elastic fibers to significantly enhance the sensitivity/Gauge factor. Also, a new method of transient thermal curing is proposed for large-scale fabrication of PDMS fibers with predefined diameters. The fiber diameter can be tuned from $\sim 10\ \mu\text{m}$ to $\sim 1000\ \mu\text{m}$. This dynamic process is investigated in detail to fabricate fibers with good uniformity.

The principle of Plateau-Rayleigh instability is utilized to modify fibers with uniformly distributed beads. These beads can tune the strain distribution along the fiber by rearranging the strain from the beads to the areas inbetween the beads – a strategy that

effectively results in strain concentration. The local strain is magnified by this process resulting in longer cracks in stretchable gold films/CNT films deposited on the surface of the fiber, and the sensitivity is significantly improved compared to fibers without beads. It was demonstrated that the beads-on-fiber stretchable strain sensor can be employed to reliably monitor sports activity. Following the strategy, other thermosetting polymer fibers could be employed to further enhance the sensitivity. It is also envisioned that the proposed strategy of strain redistribution can be applied to non-fiber-shaped stretchable strain sensors.

Figure 6.1 Proposed surface strain redistribution strategy to enhance the sensitivity of fiber-shaped sensors, and the fabrication process inspired by droplet splitting. a) FEM simulation to investigate the strain regulation effect of the micro-structured fiber as compared to the smooth fiber. b) Strain distribution along the fiber surface for the different structures in a). c) Inspired from the phenomenon of oil droplet splitting, the structured fiber in a) could be fabricated accordingly to regulate the strain distribution.

The strategy of strain redistribution is theoretically introduced to enhance the sensitivity of fiber-shaped stretchable strain sensors. It should be emphasized that for flat thin films, the most common approach to enhance the sensitivity involves manipulation of the

conductive materials itself to enable tuning of crack distribution and length,^[24, 54] film thickness,^[19] and nano/micro patterns.^[34] As for the fiber-shaped sensor, the method to enhance the sensitivity still requires to be further explored. In addition, finite element modeling (FEM) is employed to assist in the design of the strain sensors.

Figure 6.2 Tensile strain of the design structure simulated by using FEM method to indicate the strain redistribution effect by the larger volume. The modulus of the larger square region (blue region in the picture) is ten times larger than that of the fiber.

When a certain work, W , is applied to a system, the energy is absorbed/stored as the strain in the materials. The work can be written as $W = \int E \varepsilon^2 dV$, where E is the modulus, ε is the strain and V is the volume of the materials. Although the average strain is constant for a given volume under the same applied work, the local strain distribution still can be enlarged by relatively decreasing the local volume. Therefore, for the resistive stretchable strain sensors, the sensitivity can be significantly improved if the stretchable conductive materials are deposited in the region(s) where the local strain is magnified. By employing FEM it was found that the strain was indeed tuned by proper design. For example, the maximum achievable strain almost doubled by introducing an uneven distribution of microstructures along the fiber chain (Figure 6.1a, b). In addition, if high-modulus materials are employed in the low-strain (large volume) regions, the maximum strain can be further enhanced (Figure 6.2). Following this way of reasoning, the sensitivity of the fiber-shaped stretchable strain sensor can be enhanced as long as a methodology to modify the fibers with an uneven distribution of microstructures can be devised. It is well known that when oil flows along one fiber it will automatically split into droplets because of Plateau-Rayleigh instability (Figure 6.1c). Inspired by this

phenomenon, PDMS beads are produced on the PDMS fibers with the desired uneven distribution of microstructures that could take advantage of the strain redistribution effect as previously discussed (Figure 6.1c).

6.2 Experimental Methods

6.2.1 Transient curing of thermal setting polymer

As the very first step, a feasible method needs to be developed for large-scale fabrication of micrometer sized PDMS fibers. For thermoplastic polymers in general it is convenient to employ the micro-jetting method to produce fibers from the polymer melt. However, PDMS cannot be melted and jetted. Molding is an alternative method, but it was hard to fabricate fibers on micrometer length scale at reasonable cost. Inspired by Ramen, a traditional noodle processing methodology was employed to fabricate micro fibers in large quantities. There are three typical procedures to prepare Ramen noodles: dough preparation, traction by hand/machine, and cooking in boiling water. The physical concepts behind each of them are: proper viscosity adjustment, dynamic application of traction strain, and transient curing (Figure 6.3a and Figure 6.4). Herein, we used a pre-curing method to obtain the proper viscosity, followed by applying traction strain and then transient curing. The difference between the Ramen approach and ours is that boiling water cannot be used for curing of PDMS as boiling water might affect the fiber structure. In addition, PDMS is intrinsically hydrophobic making it difficult to fully immerse it in hot water. Instead, silicone oil (170 - 180 °C) was used for transient curing. It has slightly smaller density than PDMS, but its boiling point is much higher than water. Importantly, it is compatible with PDMS and can be removed easily using normal detergents. After that, micro beads were distributed automatically followed by transient curing (Figure 6.3b).

Figure 6.3 Illustration of the fabrication process of PDMS fibers with beads. a) PDMS fibers are fabricated sequentially by viscosity control, dynamic traction and transient curing in silicon oil at 170-180 °C. b) After being cleaned and dried, beads are formed according to the principle of Plateau-Rayleigh instability, by controlling the Bond number. c) By keeping other fabrication parameters constant, the fiber diameter can be tuned by adjusting the dynamic viscosity. The inset formula represents the red fitting curve. d) Influence of the dynamic viscosity of the PDMS precursor on the bead diameter. The inset red curve shows the predicted value by the theory.

6.2.2 Beads modification by Plateau-Rayleigh instability

Figure 6.4 a) As-prepared fibers were washed by the daily-used detergent followed by water and then dried in the air. b) Then after dipping with PDMS precursor, beads form automatically according to the Plateau-Rayleigh Instability. c) Finally, fibers with beads were put into the silicon oil going through the transient curing.

After the fiber fabrication process, beads was modified on the fiber to enhance the sensitivity as discussed above. Beads-on-fiber phenomena are commonly found for the nano-size fibers during the electro-spinning process,^[55-57] but only a few reports have been published for micron-sized fibers.^[58-60] Basically, beads automatically form when the viscous liquid flows along a vertically aligned fiber. The formation mechanism has been studied in detail,^[61-64] and the competition and balance between the surface tension and gravity, also called Plateau-Rayleigh instability, could explain this behavior (Figure

6.3b). The dimensionless Bond number, $G = \frac{\rho g R^3}{8\gamma h_0}$, where ρ is the density of the liquid, g is the gravitational acceleration constant, R is the diameter of the fiber, γ is the surface tension and h_0 is the undisturbed film thickness of the PDMS precursor, has been used to predict the occurrence of bead formation.^[62] According to this principle, the fiber diameter significantly affects the attachment and distribution of the beads. Normally, 0.7 is regarded as a critical value for bead formation, i.e., when G is larger than 0.7, the viscous liquid is in steady flow and beads cannot form, but for smaller G values beads do form. In order to tune the diameter of the bead, D , as discussed above, the viscosity, traction time and distance must be controlled. By applying the same traction time and distance, the effect of the viscosity on the diameter was investigated and it could be tuned from $\sim 200 \mu\text{m}$ to $900 \mu\text{m}$ (Figure 6.3d). According to theory the beads diameter can be

predicted as follows: [62]

$$H_{\max} = 1.2860c^{2/3} - 1.413 - 0.2904c^{-1/3} + O(c^{-2/3})$$

$$G = 0.5960 + 0.33c^{-2/3} + 0.19c^{-1} + O(c^{-4/3})$$

where H is the protrusion thickness of the PDMS film and $H_{\max} = (D - R) / 2$; c is the migration speed of the bead. Thus, for a given Bond number, the bead diameter can be predicted and the obtained values were in agreement with those found experimentally.

6.2.3 Stretchable active materials deposition and performance testing

In order to demonstrate that our beads-on-fiber PDMS can act as the platform to enhance the sensitivity of the strain sensor, two kinds of stretchable conductive materials were employed as the active layer. One was the stretchable gold film reported by the previous study; this film was with initial nano cracks without strain applied and these nano cracks will grow into micro cracks releasing the strain in the first strain cycle. Then subsequently, micro cracks opened and closed during the next strain cycles inducing the resistance change and achieving the stretchability of the gold film. The other one was the stretchable carbon nanotube film reported by the previous study. This film followed the same principle to achieve the stretchability. MTS model 42 was employed to apply the tensile strain. And the liquid metal (Gallium-indium eutectic, Aldrich) acted as the wire bonding adhesive which could surface the tensile strain. Keithley 4200-SCS was used to do the measurement using a sampling rate of 125 samples per second.

6.3 Principal Outcomes

6.3.1 Large-scale PDMS fiber fabrication

PDMS fibers were obtained with good uniformity along the length direction and with predefined diameters by adjusting the viscosity of PDMS and the traction time. The dynamic viscosity of PDMS was tuned by pre-curing process (Figure 6.5a) and it influenced the fiber diameter (Figure 6.3c). In order to achieve uniform fibers, for a given viscosity, the period over which the traction strain was applied need to be strictly

controlled. Considering the traction process as a viscous catenary flow under gravity, the fiber morphology could be simulated.

Figure 6.5 a) The viscosity changes with pre-curing time. b) Evolution of the fiber profile with time under gravity (within 3 seconds) by simulation using Comsol. c) The related profile at 3.4 seconds from the simulation results. d) Locally magnified region in c) to indicate the non-uniformity of the diameter of the fiber.

Figure 6.6 a) The profile changing trajectory of the fiber under gravity with different time

period. b) Experiment data of the fiber diameter uniformity. Inset illustrates the diameter measurement points on one fiber.

The beads on the fiber remained uniformly distributed during the first 3 seconds (Figure 6.5b-d). Then they gradually turned thicker in the middle and thinner near the traction point (Figure 6.5c,d, 6.6a). When the mass transfer of the viscous fluid no longer could compensate for the tensile effect inside the fiber, the fiber became thicker in the middle and non-uniform. Therefore, all fibers were immersed into the hot silicon oil bath in the first few seconds of the traction in order to obtain the fibers with relatively uniform diameter. The fibers were cut at different position along the length direction and the diameter was measured to ensure reproducible uniformity (Figure 6.6b). Moreover, the diameter of the fiber, R , also can be controlled by the amount of added PDMS, its viscosity and the traction length. A minimum diameter of about 10 μm with 4 cm in length was obtained by rapidly increasing the traction range. The length-to-diameter ratio achieved to around 4000 (Figure 6.7). The maximum fiber diameter was around 1 mm with 8 cm in length through decreasing the traction range. Importantly, by repeating this fabrication process, meters of length of the fiber can be fabricated in a short time (Figure 6.7).

Figure 6.7 a,c) Fibers with diameter of around 90 μm and 10 μm under lower magnification, and higher magnification is shown in b,d) correspondingly. e) Meters of length of the as-prepared fiber.

6.3.2 Beads modification on a single fiber and Sensitivity enhanced

One typical sample of the fiber with beads is shown in Figure 6.8a. Various active layers can be deposited on this platform including carbon nanotubes and stretchable gold films (Figure 6.8a). The stretchability of this fiber-shaped stretchable strain sensor can reach $\sim 120\%$ (Figure 6.8b). Besides, it possesses linear response with the applied strain. This sensor still remains stable after more than 5000 strain cycles under 30% tension strain (Figure 6.8c).

Figure 6.8 Beads-on-fiber stretchable strain sensors. a) The stretchable gold film was deposited onto the structured fiber. b) Resistance changes as a function of applied tensile strain. c) Long-term stability of stretchable strain sensors upon exposure to 5000 tensile strain cycles at an applied strain of 30%. d) SEM images of the stretchable gold film at different locations along the fiber. e) Statistic analysis of the crack length in d). f) Quantitative analysis of the effect of the bead protrusion height on the strain sensitivity. Inset formulas represent the fitting curve.

FEM is also employed to investigate the strain redistribution effect induced by the beads (Figure 6.8d). It is evident that the beads tune the strain distribution and induce the strain concentration, which will further determine the crack distribution of the deposited gold film. This stretchable gold film can still be conductive under the large mechanical deformation. The underlying mechanism relies on numerous randomly-distributed initial nano-cracks that develops into micro cracks to release the applied tensile strain.^[65, 66] Therefore, these micro-cracks can be taken as the tracking signal for the surface strain distribution. It is observed that cracks indeed became longer and wider at the strain concentration areas compared to those found in areas exposed to a smaller strain (Figure 6.8d). The statistical analysis also confirmed that cracks became longer than those observed in fiber without beads (Figure 6.8e). It is also worth mentioning that the resistance change was determined by the longest cracks that were more abundant of the fibers with beads. As a result, the fiber with beads possessed larger resistance change, i.e., higher gauge factor, than that without beads (Figure 6.8f). Other stretchable conductive materials can also be applied for this sensitivity-enhanced platform to fabricate fiber-shaped sensors. For example, carbon nanotubes was also employed as the conductive layer, and the sensitivity enhancement was observed and the gauge factor increased to a value around 100 (Figure 6.9 and 6.10). Moreover, since the strain can be tuned by using the platform, any active materials can be utilized to enhance the sensitivity. Thus, it opens up a new perspective to tune the sensitivity by employing a hybrid approach where the supporting elastic substrate is different from the active material itself.

Figure 6.9 a) Optical images of fibers with beads in different diameter, and the smaller one

is observed in scanning electron microscope in b).

Figure 6.10 a) Resistance changes with different strain cycles for stretchable carbon nanotube film when tensile strain of 10% is applied to the beads-on-fiber sensors. b) Sensitivity comparison of fibers with and without beads.

6.3.3 Sports motion monitoring

Finally, it was demonstrate that the fiber-shape stretchable strain sensor can be used to monitor strain induces during sports activity. A practical issue in wearable stretchable strain sensing relates to proper strain transfer from the object (muscle/joint) to the sensor. Only a few studies have been published on this aspect. The default hypothesis assumes that the object properly interfaces with stretchable strain sensor, and that the only issue worthwhile considering is the sensitivity of the sensor. However, the adaptability of the wearable sensor to the object upon deformation must be considered to ensure that the strain is accurately transferred to the sensor to avoid the signal distortion. Herein, it is reported that the interlocking effect between PDMS and textile (e.g., kinesiology tape) provides a reliable adhesion mechanism that guarantees proper strain transfer (Figure 6.11a). The PDMS precursor was half-cured and then poured onto the porous fibrous textile. Through the mechanical test, the strength of the junction area of PDMS and textile is larger than that of PDMS itself (Figure 6.11a). Moreover, the kinesiology tape is a good candidate to support the stretchable strain sensor. It adheres tightly and conformably to skin and is insensitive to the sweat. Integrated with the customized chip, the data was recorded wirelessly (Figure 6.11b,c). The gesture of squatting and leg lifting was successfully monitored (Figure 6.11d,e). It is envisioned that the fiber-shaped sensors can be further integrated with other fiber-shaped

batteries/super-capacitors to achieve the smart textile in the near future for potential healthcare, rehabilitation and sports monitoring and so forth.

6.4 Conclusions

In summary, the new beads-on-fiber stretchable strain sensor is reported based on the principle of Plateau-Rayleigh instability and the novel strategy of the strain redistribution through delicate structure designs to enhance the sensitivity of the fiber-shaped stretchable strain sensor is proposed. a new large-scale PDMS fiber fabrication method is also reported inspired by the traditional noodle preparation process. The fiber diameter and the diameter uniformity along the length direction can be well controlled. The fiber-shaped stretchable strain sensors can be reliably used to monitor the sports activity. Following the strategy, the sensitivity of the fiber-shaped stretchable strain sensor could be further enhanced and other thermosetting polymer based fiber sensors can be fabricated. Also, the proposed strategy to enhance the sensitivity could be applied to non-fiber-shaped stretchable strain sensors.

Figure 6.11 Demonstration of the beads-on-fiber stretchable strain sensor for sports monitoring. a) Adhesion test of the PDMS film and the kinesiology tape. Reliable attachment was achieved by interlocking effect of the PDMS and the tape. b) The sensor with the tape was adhered onto the joint of lower limb to monitor the squatting. c) Detailed description of the wireless resistance monitoring chip. Also, the sensor can be used to monitor the leg lifting. d,e) The typical raw data obtained by the fiber-shaped sensor when detecting squatting and leg lifting. The noise was induced by the limb natural vibration.

References:

- [1] S. Lee, Y. Inoue, D. Kim, A. Reuveny, K. Kuribara, T. Yokota, J. Reeder, M. Sekino, T. Sekitani, Y. Abe, T. Someya, *Nature Commun.* **2014**, *5*, 5898.
- [2] K. K. Kim, S. Hong, H. M. Cho, J. Lee, Y. D. Suh, J. Ham, S. H. Ko, *Nano Lett.* **2015**, *15*, 5240.
- [3] M. Amjadi, K. U. Kyung, I. Park, M. Sitti, *Adv. Funct. Mater.* **2016**, *26*, 1678.
- [4] J. Park, I. You, S. Shin, U. Jeong, *ChemPhysChem* **2015**, *16*, 1155.
- [5] D. Qi, Z. Liu, W. R. Leow, X. Chen, *MRS Bulletin* **2017**, *42*, 103.
- [6] X. Chen, *Small Methods* **2017**, *1*, DOI: 10.1002/smtd.201600029.
- [7] W. Zeng, L. Shu, Q. Li, S. Chen, F. Wang, X. M. Tao, *Adv. Mater.* **2014**, *26*, 5310.
- [8] L. M. Castano, A. B. Flatau, *Smart Mater. Struct.* **2014**, *23*, 053001.
- [9] M. Hamed, L. Herlogsson, X. Crispin, R. Marcilla, M. Berggren, O. Inganäs, *Adv. Mater.* **2009**, *21*, 573.
- [10] F. Carpi, D. De Rossi, *IEEE Trans. Inf. Technol. Biomed.* **2005**, *9*, 295.
- [11] K. Cherenack, C. Zysset, T. Kinkeldei, N. Münzenrieder, G. Tröster, *Adv. Mater.* **2010**, *22*, 5178.
- [12] L. Hu, M. Pasta, F. L. Mantia, L. Cui, S. Jeong, H. D. Deshazer, J. W. Choi, S. M. Han, Y. Cui, *Nano Lett.* **2010**, *10*, 708.
- [13] X. Pu, L. Li, H. Song, C. Du, Z. Zhao, C. Jiang, G. Cao, W. Hu, Z. L. Wang, *Adv. Mater.* **2015**, *27*, 2472.
- [14] S. Seyedin, J. M. Razal, P. C. Innis, A. Jeiranikhameneh, S. Beirne, G. G. Wallace, *ACS Appl. Mater. Interfaces* **2015**, *7*, 21150.
- [15] D. Zhang, M. Miao, H. Niu, Z. Wei, *ACS Nano* **2014**, *8*, 4571.
- [16] Z. Wang, Y. Huang, J. Sun, Y. Huang, H. Hu, R. Jiang, W. Gai, G. Li, C. Zhi, *ACS Appl. Mater. Interfaces* **2016**, *8*, 24837.
- [17] G. Cai, J. Wang, K. Qian, J. Chen, S. Li, P. S. Lee, *Adv. Sci.* **2016**, doi: 10.1002/advs.201600190.
- [18] T. Yamada, Y. Hayamizu, Y. Yamamoto, Y. Yomogida, A. Izadi-Najafabadi, D. N. Futaba, K. Hata, *Nature Nanotech.* **2011**, *6*, 296.
- [19] E. Roh, B.-U. Hwang, D. Kim, B.-Y. Kim, N.-E. Lee, *ACS Nano* **2015**, *9*, 6252.
- [20] Z. Liu, D. Qi, P. Guo, Y. Liu, B. Zhu, H. Yang, Y. Liu, B. Li, C. Zhang, J. Yu, B.

- Liedberg, X. Chen, *Adv. Mater.* **2015**, 27, 6230.
- [21] Z. Liu, X. Wang, D. Qi, C. Xu, J. Yu, Y. Liu, Y. Jiang, B. Liedberg, X. Chen, *Adv. Mater.* **2017**, 27, 1603382.
- [22] R. Rahimi, M. Ochoa, W. Yu, B. Ziaie, *ACS Appl. Mater. Interfaces* **2015**, 7, 4463.
- [23] J. Guo, X. Liu, N. Jiang, A. K. Yetisen, H. Yuk, C. Yang, A. Khademhosseini, X. Zhao, S. H. Yun, *Adv. Mater.* **2016**, 28, 10244.
- [24] J. Zhong, Q. Zhong, Q. Hu, N. Wu, W. Li, B. Wang, B. Hu, J. Zhou, *Adv. Funct. Mater.* **2015**, 25, 1798.
- [25] F. Guo, X. Cui, K. Wang, J. Wei, *Nanoscale* **2016**, 8, 19352.
- [26] M. Amjadi, M. Turan, C. P. Clementson, M. Sitti, *ACS Appl. Mater. Interfaces* **2016**, 8, 5618.
- [27] J. C. Yeo, H. K. Yap, W. Xi, Z. Wang, C. H. Yeow, C. T. Lim, *Adv. Mater. Tech.* **2016**, 2, 2016.
- [28] Y. Cheng, R. Wang, J. Sun, L. Gao, *Adv. Mater.* **2015**, 27, 7365.
- [29] Q. Liu, J. Chen, Y. Li, G. Shi, *ACS Nano* **2016**, 10, 7901.
- [30] Q. Li, Z. Ullah, W. Li, Y. Guo, J. Xu, R. Wang, Q. Zeng, M. Chen, C. Liu, L. Liu, *Small* **2016**, 12, 5058.
- [31] C. Wang, X. Li, E. Gao, M. Jian, K. Xia, Q. Wang, Z. Xu, T. Ren, Y. Zhang, *Adv. Mater.* **2016**, 28, 6640.
- [32] L. Cai, L. Song, P. Luan, Q. Zhang, N. Zhang, Q. Gao, D. Zhao, X. Zhang, M. Tu, F. Yang, *Sci. Rep.* **2013**, 3, 3048.
- [33] D. J. Lipomi, M. Vosgueritchian, B. C. Tee, S. L. Hellstrom, J. A. Lee, C. H. Fox, Z. Bao, *Nature Nanotech.* **2011**, 6, 788.
- [34] C. Yan, J. Wang, W. Kang, M. Cui, X. Wang, C. Y. Foo, K. J. Chee, P. S. Lee, *Adv. Mater.* **2014**, 26, 2022.
- [35] J. T. Muth, D. M. Vogt, R. L. Truby, Y. Mengüç, D. B. Kolesky, R. J. Wood, J. A. Lewis, *Adv. Mater.* **2014**, 26, 6307.
- [36] X. Xiao, L. Yuan, J. Zhong, T. Ding, Y. Liu, Z. Cai, Y. Rong, H. Han, J. Zhou, Z. L. Wang, *Adv. Mater.* **2011**, 23, 5440.
- [37] Q. Sun, W. Seung, B. J. Kim, S. Seo, S. W. Kim, J. H. Cho, *Adv. Mater.* **2015**, 27, 3411.
- [38] G.-H. Lim, N.-E. Lee, B. Lim, *J. Mater. Chem. C* **2016**, 4, 5642.

- [39] Y. Pang, H. Tian, L.-Q. Tao, Y. Li, X. Wang, N.-q. Deng, Y. Yang, T.-L. Ren, *ACS Appl. Mater. Interfaces* **2016**, 8, 26458.
- [40] G. Shi, Z. Zhao, J. H. Pai, I. Lee, L. Zhang, C. Stevenson, K. Ishara, R. Zhang, H. Zhu, J. Ma, *Adv. Mater.* **2016**, 26, 7614.
- [41] G.-F. Yu, X. Yan, M. Yu, M.-Y. Jia, W. Pan, X.-X. He, W.-P. Han, Z.-M. Zhang, L.-M. Yu, Y.-Z. Long, *Nanoscale* **2016**, 8, 2944.
- [42] B.-U. Hwang, J.-H. Lee, T. Q. Trung, E. Roh, D.-I. Kim, S.-W. Kim, N.-E. Lee, *ACS Nano* **2015**, 9, 8801.
- [43] M. Amjadi, A. Pichitpajongkit, S. Lee, S. Ryu, I. Park, *ACS Nano* **2014**, 8, 5154.
- [44] S. G. Yoon, H.-J. Koo, S. T. Chang, *ACS Appl. Mater. Interfaces* **2015**, 7, 27562.
- [45] J. J. Park, W. J. Hyun, S. C. Mun, Y. T. Park, O. O. Park, *ACS Appl. Mater. Interfaces* **2015**, 7, 6317.
- [46] M. Park, J. Im, J. Park, U. Jeong, *ACS Appl. Mater. Interfaces* **2013**, 5, 8766.
- [47] J. Lee, S. Kim, J. Lee, D. Yang, B. C. Park, S. Ryu, I. Park, *Nanoscale* **2014**, 6, 11932.
- [48] H. J. Sim, C. Choi, S. H. Kim, K. M. Kim, C. J. Lee, Y. T. Kim, X. Lepró, R. H. Baughman, S. J. Kim, *Sci. Rep.* **2016**, 6, 35153.
- [49] J. Ge, L. Sun, F. R. Zhang, Y. Zhang, L. A. Shi, H. Y. Zhao, H. W. Zhu, H. L. Jiang, S. H. Yu, *Adv. Mater.* **2015**, 28, 722.
- [50] H. Wang, Z. Liu, J. Ding, X. Lepró, S. Fang, N. Jiang, N. Yuan, R. Wang, Q. Yin, W. Lv, *Adv. Mater.* **2016**, 28, 4998.
- [51] A. Frutiger, J. T. Muth, D. M. Vogt, Y. Mengüç, A. Campo, A. D. Valentine, C. J. Walsh, J. A. Lewis, *Adv. Mater.* **2015**, 27, 2440.
- [52] S. Chen, Z. Lou, D. Chen, K. Jiang, G. Shen, *Adv. Mater. Tech.* **2016**, doi: 10.1002/admt.201600136.
- [53] S. Zhu, J. H. So, R. Mays, S. Desai, W. R. Barnes, B. Pourdeyhimi, M. D. Dickey, *Adv. Mater.* **2013**, 23, 2308.
- [54] D. Kang, P. V. Pikhitsa, Y. W. Choi, C. Lee, S. S. Shin, L. Piao, B. Park, K.-Y. Suh, T.-i. Kim, M. Choi, *Nature* **2014**, 516, 222.
- [55] X. Li, R. Zhang, W. Yu, K. Wang, J. Wei, D. Wu, A. Cao, Z. Li, Y. Cheng, Q. Zheng, *Sci. Rep.* **2012**, 2, 870.
- [56] G. Eda, S. Shivkumar, *J. Appl. Polym. Sci.* **2007**, 106, 475.
- [57] W. Zuo, M. Zhu, W. Yang, H. Yu, Y. Chen, Y. Zhang, *Polym. Eng. & Sci.* **2005**, 45,

704.

[58]H. Fong, I. Chun, D. Reneker, *Polymer* **1999**, *40*, 4585.

[59]Y. Chen, Y. Zheng, *Nanoscale* **2014**, *6*, 7703.

[60]S. Feng, Y. Hou, Y. Chen, Y. Xue, Y. Zheng, L. Jiang, *J. Mater. Chem. A* **2013**, *1*, 8363.

[61]X. Tian, H. Bai, Y. Zheng, L. Jiang, *Adv Funct. Mater.* **2011**, *21*, 1398.

[62]L. Yu, J. Hinch, *J. Fluid Mech.* **2013**, *737*, 232.

[63]Z. Ding, J. Xie, T. N. Wong, R. Liu, *J. Fluid Mech.* **2014**, *752*, 66.

[64]P. P. Bhat, S. Appathurai, M. T. Harris, M. Pasquali, G. H. McKinley, O. A. Basaran, *Nature Phys.* **2010**, *6*, 625.

[65]Z. Liu, M. Yu, J. Lv, Y. Li, Z. Yu, *ACS Appl. Mater. Interfaces* **2014**, *6*, 13487.

[66]S. P. Lacour, S. Wagner, Z. Huang, Z. Suo, *Appl. Phys. Lett.* **2003**, *82*, 2404.

Chapter 7

High-adhesion stretchable electrodes by nanopiles interlocking*

Stretchable electronics is vital for the bio-integration of electronic components and biology, such as soft exoskeleton systems, human-machine interfaces, and implantable bioelectronics. Adhesion is crucial for the long-term use of stretchable devices, such as the detection of body-surface bio-signals in electromyography and electrocardiography, and implanted devices. However, the particular combination of materials to fabricate the stretchable electrodes faces one intrinsic problem related to interfacial adhesion, especially for the thin film electrode on elastic substrate. This is due to the huge difference in physical and chemical properties (e.g., Young's modulus: tens of GPa for gold while only several MPa for PDMS) between the conductive material and the elastic substrate. In this work, inspired by a tree, a new strategy – nanopile interlocking - is proposed to fabricate high-adhesion stretchable electrodes that can be used as strain sensors with tunable stretchability, high gauge factor and stability. The nanopile not only provides the interlocking effect to significantly improve the adhesion, but also ensures that the tensile strain in the film is redistributed to release the strain energy by random cracks forming the connecting network and achieving the stretchability.

*Published substantially as Liu et al., High-adhesion Stretchable Electrodes Based on Nanopile Interlocking, *Adv. Mater.* **2017**, **27**, 1603382.

7.1 Introduction

Stretchable electronics is vital for the bio-integration of electronic components and biology,^[1-5] such as soft exoskeleton systems,^[6] human-machine interfaces,^[7-9] and implantable bioelectronics.^[10-12] As core units, stretchable electrodes and strain sensors provide the fundamental platform for investigating the electrophysiology of tissues *in vivo/vitro* as well as mechanical deformation in medical therapy and tissue engineering.^[13-30] Since naturally there is nearly no intrinsic stretchable materials that is fully conductive, several strategies have been proposed to achieve the stretchability including spring-inspired principles,^[31-36] nanoparticle polymer composites,^[37-40] liquid assemblies^[41-43] and crack-based thin films.^[44-49] The strategies are diverse, but the overwhelming majority of the methodologies are based on various combinations of inorganic conductive materials (e.g. metals and carbon) and organic elastic polymers (e.g. polydimethylsiloxane (PDMS) and polyurethane).

These particular combination of materials faces one intrinsic problem related to interfacial adhesion, especially for the thin film electrode on elastic substrate. This is due to the huge difference in physical and chemical properties (e.g., Young's modulus: tens of GPa for gold while only several MPa for PDMS) between the conductive material and the elastic substrate.^[50-61] Adhesion is crucial for the long-term use of stretchable electronics, such as the detection of body-surface bio-signals in electromyography (EMG) and electrocardiography (ECG), and implanted devices where the interface friction may easily induce failures of debonding.^[62, 63] Thus, one overarching materials challenge is to simultaneously obtain electrodes with desirable stretchability and high adhesion to the supporting polymer substrate.

Figure 7.1 Proposed concept of nanopile interlocking to simultaneously achieve high adhesion and large stretchability. a) Diagram illustrating to show the principle of a tree standing firmly on the ground by stretching fractal roots into the soft soil. b) High-adhesion model. c) Inspired by it, just like piling process used in building, nanopiles are fabricated under the metal film to form the interlocking layer (equivalent to the transition layer in b)) between metal film and elastic polymer. d,e) FEM simulations of the strain distribution in the film with and without nanopiles under the tensile strain of 10%. f) Strain distribution along the dashed black lines in d, e).

Inspired by the plants, like trees, standing firmly on the ground by stretching out fractal roots underneath (Figure 7.1a-c), an interlocking layer could be introduced by growing biomimetic roots under the electrode to significantly enhance the adhesion. More importantly, it is also desired that the roots extending into the soft substrate could regulate the strain distribution in the metal film thus avoiding throughout cracks induced by the strain concentration. It needs to be stressed that the strain energy is transferred from the elastic substrate to the top rigid metal film. So the manner how it is transferred through the interface between the metal film and elastic substrate is crucial for the performance

of the electrode. Compared with the traditional flat film without any special structure design underneath, the strain in the film with roots would be transferred from the substrate to the biomimetic root layer first and then to the metal film on top. The metal roots are much more rigid than the soft substrate, and could efficiently regulate strain distribution in the metal film. The finite element modeling (FEM) results show that the roots or pile array underneath can indeed change the strain distribution into a more random style inside the film compared with that in flat film without pile array (Figure 7.1d-f). Therefore, a kind of nanopile structure could be constructed to create an interlocking layer that offers both high adhesion and stretchability.

Herein, a new strategy - nanopile interlocking - is reported to fabricate high-adhesion stretchable electrodes that can also be used as strain sensors with tunable stretchability, high gauge factor and stability. The nanopile not only provides an interlocking effect to significantly improve the adhesion, but also ensures that the tensile strain in the film is redistributed to release the strain energy by randomly distributed cracks forming the connection network and achieving the stretchability. The adhesion is significantly improved by over an order of magnitude compared to stretchable thin gold film with initial nanocracks and non-stretchable flat gold film. The stretchability of the electrode can reach $\sim 50\%$ which is more than enough for the body-surface measurements that typically encounter deformations up to $\sim 30\%$.^[64] As a proof of concept, it is demonstrated that the stretchable electrode can be used to detect EMG signals and that the stretchable strain sensor can be utilized to simultaneously monitor the deformation induced by the elbow bending. The strategy provides a new perspective to achieve stretchability that is vital for stretchable electronics. It also opens up for exploration of the advanced property-function relationships combining high adhesion and stretchability.

7.2 Experimental Methods

7.2.1 Nanopiles growth

Anodic aluminum oxide (AAO) templates purchased from Whatman, Singapore and Puyuan Nano, China with the pore size of around 100 nm were directly thermally evaporated with gold film of different thickness from 30 nm to 500 nm without any pre-treatment. The vacuum was around 1.5×10^{-6} Torr, the evaporation rate was $0.5 \text{ \AA s}^{-1}$

and the distance from the gold source to the target was around 8 cm. The target tray rotated in 10 rpm. Then, the template, as the working electrode and with Pt and Ag/AgCl as the counter and reference electrodes, was electro-deposited with gold nanopile with different length by controlling the deposition time. The electroplating solution was the commercialized Au Orotamp 24 (Technic Inc.) and the potential bias used was -0.95 V. After that, AAO templates were adhered with Cu tape and then adhered to the glass petri dishes by double-side carbon tape. AAO templates were removed by 3 mol L⁻¹ NaOH solution completely followed by DI water washing and natural drying. The PDMS with the 1:10 weight ratio of the cross linker and monomer was diluted with hexane. The weight ratio of PDMS and hexane was 3:7. The pervious samples underwent oxygen plasma treatment and then were poured with the diluted PDMS immediately. The samples were put into vacuum for two hours when the diluted PDMS gradually went into the gaps among the nanopiles and hexane evaporated away at the same time. Lastly, they completed the polymerization in the oven at 80 °C. Fabricated samples can be peeled off from the Cu tape with the adhesive materials transferred from Cu film to the gold film which already indicated the good adhesion achieved (Figure 7.2).

Figure 7.2 Diagram to illustrate the fabrication process of stretchable gold film with nanopiles. The green color shown for the Cu tape represents the adhesive material on the Cu film that is totally transferred to gold film after peeling off the sample from the Cu tape indicating the good adhesion of the sample.

7.2.2 Adhesion testing

The tensile adhesion strength and adhesion ratio were used to quantitatively reflect the adhesion following the well-developed testing process. The samples were adhered to the cylindrical wood sticks by epoxy resin. The tensile machine used here was MTS C42 with 50 N load cell and 100 N Bionix vice grips. The adhesion ratio was calculated by the area ratio of the left gold film to the initial gold film. In addition, dynamically synchronous resistance and impedance measurement under uniaxial strain was conducted as reported previously^[45].

7.2.3 EMG monitoring

EMG signal and the deformation induced by the elbow bending were measured at the same time all by the fabricated stretchable units. Two working electrodes were placed on the biceps and one reference electrode was held in hand. Two ends of the stretchable strain sensor were adhered to two sides of the elbow. EMG signal was amplified and pre-treated by the commercialized device and software (*Backyard Brains*). The signal was further analyzed in Matlab by using an opencode.^[73]

7.3 Principal Outcomes

7.3.1 High-adhesion stretchable electrodes

In a typical experiment, anodic aluminum oxide (AAO) membrane was employed as a template to electrochemically fabricate the metallic nanopile array.^[65, 66] Then the template was dissolved after fixing the surface on the copper tape with acrylic adhesive as the adhesion layer, followed by the oxygen plasma treatment. Diluted PDMS was poured onto the nanopile structure and cured in the vacuum. Finally, the fabricated sample was peeled off from the copper tape (Figure 7.3). During this process the acrylic adhesive on the copper tape was totally transferred onto the metal surface, suggesting that the adhesion between the metal film and the elastic polymer was even higher than that between the copper and the acrylic film (Figure 7.4). However, most of the normal stretchable gold film prepared by the crack-induced principle would detach from the polymer after peeling off the copper tape (Figure 7.5). It was also evident that the piling structure had been successfully inserted into the elastic substrate (Figure 7.3a). Finally,

the acrylic layer was removed in acetone. As control experiments, normal crack-based stretchable gold film (CSGF)^[67] and dense non-stretchable gold film (NSGF) were prepared by employing the commonly-used adhesion enhancement method, i.e., with 10 nm-thickness chromium as the adhesive layer for both.

Figure 7.3 Adhesion enhancement and stretchability achieved by the nanopile and corresponding principles behind. a) Cross-section view of the fabricated stretchable gold film with nanopiles penetrating into the PDMS substrate. Insets show the front and reverse sides of the samples. The reverse is in black color induced by the absorption effect of the nanopile. b) Adhesion comparison of the nanopile film with normal crack-based stretchable gold film and flat non-stretchable film. c,d) Adhesion and stretchability performance with different film thickness for a given nanopile length of 1.5 μm , and different nanopile length for a given film thickness of 300 nm (inserts). e-i) FEM simulation to investigate the effect of film thickness and nanopile length on the strain distribution in the film under the tensile strain of 10%.

Figure 7.4 Images to show the fabricated samples. a, b) The effect of the adhesive material transferred from the copper tape to the gold film.

Figure 7.5 Images to contrastively illustrate the adhesion problem of the normal crack-based stretchable gold film. a,b) The front and back side of the CSGF (left) and stretchable gold film with nanopiles (right). The back side shows typical yellow color for CSGF and black color for the nanopile film. c,d) The adhesion test by using Cu tape for film with nanopiles. Only a small amount of the film is removed by the tape. However, almost all gold film is removed for the CSGF sample showed in e,f).

The so-prepared samples underwent the standard testing process under tensile strain to quantitatively evaluate the adhesion strength by using a rigid rod with epoxy resin as the glue (Figure 7.6a).^[68-70] The peeling stress, σ_a , and the area ratio (the remaining metal film to the original film), S_a , were measured and calculated. It was found that S_a was > 95% for samples with nanopiles but only 13% and < 5% for NSGF and CSGF films, respectively, indicating a significant improvement of the adhesion to the elastic nanopile substrate. When the rigid rod with the epoxy resin was peeled off from the metal surface, the overall stress was calculated to be ~ 2.6 MPa which only took off < 5% of the gold film with nanopiles underneath, showing that the adhesive strength of the weakest part was around 2.6 MPa and the actual strength was larger than that between the epoxy resin and gold film. Notably, the strength was only ~ 0.25 MPa for CSGF and NSGF (Figure 7.3b). Undoubtedly, the strategy can improve the adhesion strength at least an order of magnitude. Scotch tape was employed to intuitively illustrate the enhancement effect (Figure 7.6b-i). Obviously, all CSGF was easily removed from the substrate by the tape, whereas the gold film with nanopile underneath appeared to adhere strongly to the substrate.

Figure 7.6 Images to show the adhesion test process by using tensile in a) and tape method in for the sample with nanopiles in b-e) and the CSGF sample in f-i), respectively. The adhesive material on the scotch tape is even transferred to the gold film in d) indicating the excellent adhesion property for the sample with nanopiles. Nearly all gold film is removed by the tape for CSGF.

The surface morphology of the removed part was investigated to reveal the fracture principle of the films with nanopiles. A small portion of nanopiles was missing and small amount of residual PDMS was found on the nanopiles (Figure 7.7a,b). Thus, the debonding was not exclusively induced by the nanopile detachment but also by cohesive failure of PDMS, which indeed points towards a strong nanopile interlocking effect. Besides, crack-based stretchable carbon nanotube film was fabricated as the control sample.^[45] It was found that the adhesion of the CNT film (functionalized with carboxylic acid group) with oxygen plasma treated PDMS was only about half of that of nanopile samples, but it was larger than that of crack-based stretchable gold film due to the hydrogen bond interaction (Figure 7.7c,d). Additionally, the effect of the density of nanopiles on the performance was investigated (Figure 7.8). It showed that the adhesion decreased but the stretchability increased with the decrease of the porosity, indicating that the nanopile became loose which benefitted the stretchability. However, it is also predicted that if it is too loose, the stretchability would also decrease because the extreme condition is that there is totally no nanopile underneath.

Figure 7.7 SEM images showing the fracture mechanism of the sample with nanopiles. It is clearly shown that part of PDMS is left among the nanopiles and that some of the piles are removed, indicating a good interlocking effect between the nanopiles and PDMS substrate. Additionally, the adhesion test was also conducted for stretchable CNT electrodes in c) and d).

Furthermore, the effect of nanopile length and metal thickness on the adhesive strength was investigated in detail. The S_a increased with increasing nanopile length in a linear manner. This was not an unexpected finding since the adhesion strength is mainly decided by the contacting area between the nanopiles and the polymer. However, only small changes in S_a was seen with increasing metal film thickness (Figure 7.3c). Interestingly, when the effect of nanopile length on the stretchability was investigated, it was found that the stretchability decreased sharply for short pile lengths $< 0.5 \mu\text{m}$, followed by a partial recovery in stretchability with lengths $> 0.5 \mu\text{m}$ (Figure 2d insert). Moreover, the stretchability increased monotonically with increasing thickness up to about 400 nm above which it started to decrease (Figure 7.3d). In addition, it should be noticed that it is hard to achieve both the maximum stretchability and largest adhesion simultaneously (Figure 7.3c,d), but the stretchability can achieve to $> 30\%$ which satisfied the basic requirement for the skin surface bio-signal detection^[64] and the adhesion ratio can be larger than 85% when the film thickness and nanopile length is larger than or equal to 300 nm and 0.5 μm , respectively.

Figure 7.8 The investigation of the effect of the porosity on the performance. a,b) SME images of two different AAO template with similar pore size but different porosity. c,d) Corresponding treatment by using open-code software Imagej to calculate the porosity. e) Stretchability and adhesion test with different porosity.

Figure 7.9 Images illustrating the unique feature of the crack-based principle to achieve stretchability. a) Front view of the NSGF and CSGF sample with the initial defect observed by optical microscope in b). c-e) The defect in the NSGF is the origin of the throughout cracks breaking the conductive path under strain. However, since the NSGF is based on the crack-based principle to achieve stretchability, the defect will not induce any strain concentration inside the film in f-h), although the defect already blocks more than half of the film, and the film still keeps conductive under strain.

In order to gain a deeper understanding of the mechanism, the crack-based principle to achieve stretchable conducting materials was investigated in detail. As mentioned earlier, the crack-based one releases the strain energy by numerous randomly distributed micro cracks, whereas the non-stretchable flat film does it via the throughout cracks that cut off the conducting path. Moreover, films with randomly distributed micro cracks display small changes in surface morphology during stretching in contrast to the non-stretchable film with the throughout cracks (Figure 7.9a,b). One unique feature of micro crack-based stretchable conducting films is that they are insensitive to the presence of defects in the metal film. The stretchable films, such as those fabricated based on spring-like strategy, on the other hand, are indeed sensitive to defects introduced during fabrication and/or

subsequent manipulation/treatment (Figure 7.9c-e). For example, such defects serve as nucleation points for throughout cracks because of local strain concentration. On the contrary, crack-based stretchable metal films do not suffer from strain concentration because the strain energy already has been released by the random micro cracks inside the film. Although the presence of defect removes some of the micro cracks, the film still remains stretchable and conductive (Figure 7.9f-h). Since micro cracks normally form during the first cycle of the tensile strain, randomly distributed seeds in the film might assist in the formation of micro cracks. Therefore, two parameters are proposed to determine the overall stretchability/conductivity of the film: 1) the initial surface morphology of the film (decided by the film growth condition) determining the origin of the micro cracks; and 2) the nanopiles penetrating into PDMS regulating the strain distribution in the film.

Figure 7.10 SEM images illustrating the growth process of the gold film on AAO template. a-d) Different thickness of the gold film is deposited: 30, 50, 100, 300 nm respectively. Two typical features are observed: the grain size is relatively large (compare with Au film on glass, Figure S9c, d) and the morphology still reveals a porous state even for 300 nm thick films.

Figure 7.11 AFM images in amplitude mode (a-b) and phase mode (c-d) to clearly and quantitatively reflect the surface grain distribution. The grain size is as large as 200 nm and the porous-like state is evident.

The influence of the surface morphology on the gold film evaporation and the electrochemical deposition processes on top of and within the AAO were investigated. For example, it is well-known that the physical and chemical properties of substrate surface, such as surface roughness and surface energy, govern the film growth during the gold evaporation process. It was found that the texture and grain distribution of the initially formed gold film was guided by the surface morphology of the porous AAO film. Relatively large nanoparticle-like feature appeared during the evaporation process that finally resulted in a morphology consisting of coarse grains (Figure 7.10 and 7.11). Under the same growth condition, these grains were found to be much larger (~ 250 nm)

(Figure 7.12a,b) than those observed for films grown on glass (~ 40 nm) (Figure 7.12c,d), indicating that the gold film on AAO is less dense and porous in nature. Furthermore, the apertures surrounded by larger grains (Figure 7.12a,b) might serve as starting points (seeds) for the micro crack-formation during initial stretching.

Figure 7.12 SEM images of the gold film deposited on AAO template (a-b) and glass slide (c-d) under the same film growth condition showing the totally different grain size and morphology. The one on AAO is much larger than that on glass and most importantly, the porous state remains for that on AAO, but there is not for the flat gold film on glass.

Figure 7.13 SEM images to investigate the film transition before and after electrochemical deposition. a) a relatively thin film (80 nm) is deposited on AAO templated, and the porous state is kept. However, all pores are sealed after the electrochemical deposition and before forming the nanopiles underneath.

The electrochemical deposition process is also important for the final outcome as it would change the surface morphology of the nanopile metal film. The electrolyte penetrates the AAO template and seals the pores prior to formation the nanopile structure. From the top view of thin gold film, it can be clearly seen that the overall film appearance changes from mesh-like morphology into a dense film (Figure 7.13). Therefore, for small nanopile thickness ($< 1.5 \mu\text{m}$), the apertures in the gold film were sealed by the electrochemical deposition resulting in a dense film that decreased the stretchability. Notably, the film still possessed a stretchability of more than 15% due to the strain regulation effect of the nanopiles (Figure 7.3d). With increasing thickness, the apertures inside the evaporated gold film were less affected by the electrochemical deposition process which resulted in improved stretchability most likely because of micro crack formation. However, if the film was too thick (up to 500 nm in thickness), although there were still initial apertures in the upper layer, the strain regulation of the nanopile tended to disappear in agreement with the FEM simulation (Figure 7.3e-g), resulting in a less stretchable film. For a certain nanopile length (e.g. 1.5 μm), the strain distribution was relatively random when the film thickness is smaller. It can be clearly seen that there was less strain on top of the nanopile dividing the strain concentration inside the film, which can be called “regulation effect” of the nanopile (Figure 7.3e). However, the strain distribution tended to be homogenous with the increase of the film thickness (Figure 7.3f, g) indicating that the regulation effect weakened. For a certain film thickness, when decreasing nanopile length, as shown by the FEM simulation (Figure 7.3e, h and i), the strain distribution tended to be homogenous, regulation effect weakened and the stretchability decreased. Therefore, for a thin gold film ($\sim 300 \text{ nm}$) and short nanopiles ($< 0.5 \mu\text{m}$), the apertures were sealed without the strong strain regulation from the nanopile, which induced the sharp decrease of the stretchability (insert Figure 7.3d).

Figure 7.14 Mechanism of the stretchability and resistance change of the stretchable strain sensor. a-b) Surface morphology of the gold film with nanopiles under tensile strain of 0% and 30%, respectively. As comparison, the non-stretchable gold film under tensile strain of 30% is illustrated in c). d) The typical resistance change of stretchable gold film with nanopiles and non-stretchable gold film. It indicates the fracture of the film when the resistance is beyond the detection limit. e) Statistic analysis of the crack length in b, c). f) Resistance change under different applied tensile strain with more than 1000 cycles. The DC resistance changes in the small scale from around 5.5 Ω to 12.5 Ω which is only 1% of the interface impedance of the electrode, which has little effect on the EMG signal detection but can be utilized to detect strain.

The surface morphology of the metal film under strain was also investigated in order to further understand the mechanism of the stretchability (Figure 7.14a-c). The cracks were aligned perpendicular to the strain direction for both the nanopile and NSGF samples. However, it was obvious that much longer cracks were formed in the NSGF sample than those in the corresponding nanopile film. And the NSGF film turned to be non-conductive almost with the immediate effect when applied tensile strain (Figure 7.14d). Moreover, quantitative analysis confirmed a narrow distribution of short cracks in the nanopile film (Figure 7.14e). In addition, the crack edge rolled up induced by the weak adhesion in the NSGF, but it did not happen for nanopile film due to the good adhesion (Figure 7.14c). Furthermore, benefiting from the growth mode on AAO and the regulation effect of the nanopile, the thickness of the metal film can be as large as 500 nm when the film still kept stretchability. This cannot be obtained with CSGF that requires a film of much smaller thickness < 100 nm.^[67] The thicker film also significantly reduced the initial resistance to $\sim 5.5 \Omega$, a value that changed to $\sim 12.5 \Omega$ under tensile strain of 10%. Both values were relatively low in comparison to the impedance of the same electrode in EMG monitoring $\sim 1300 \Omega$ (at several hundred Hz) (Figure 7.15a). Thus, the resistance change would not have significant effect on the EMG signal detection. This resistance change can be also employed to detect tensile strain ($GF \sim 12.5$). Herein, gauge factor (GF), corresponding to the sensitivity of the strain sensor, is defined as $\Delta R/R_0/\Delta \varepsilon$, where R_0 is the initial resistance and ε is the strain applied. The performance of this stretchable strain sensor was quite stable even after one thousand cycles, and it showed a linear response (Figure 7.14f). Stretchable silver electrodes (Figure 7.16) following the strategy indicating that it can apply to various metals.

Figure 7.15 a) Impedance of the electrode. At about 100 Hz, the impedance is around 1000 Ω which is much larger than the DC resistance of the electrode ($\sim 10 \Omega$). b) By using this electrode, the EMG signal can be detected and the amplitude spectrum analyzed.

Figure 7.16 High-adhesion stretchable silver electrodes based on this strategy. AAO template deposited with a) gold and b) silver. c) Following the similar fabrication procedure, stretchable silver electrode was fabricated.

7.3.2 EMG and mechanical strain monitoring

As a proof of concept, it is demonstrate that the fabricated stretchable gold films following this strategy can be used both for the detection of EMG signals and strain induced by the elbow bending (Figure 7.17a). EMG is an important bio-signal vital for constructing invasive human-machine interface^[71] and can be extensively utilized for soft robotic control, exoskeleton systems and in wearable assistive healthcare devices.^[72] Accurate prediction of the human motion unfortunately cannot be achieved only by exclusively monitoring EMG signals, as they tend to suffer from electrode-bio interface failures and/or external mechanical noise.^[18] Normally, there would be strain generation in the skin surface or near joint with the muscle contraction. Thus, strain detection and EMG monitoring can be combined to obtain accurate motion information. Long-term monitoring always involves friction between the skin and the electrode. Herein, the long-term friction was simulated by cyclic friction test in short time (300 cycles in around 10 mins) by using PDMS with a rough surface and a CSGF sample was used as control. The resistance changes matched well with the elbow bending (Figure 7.18a), and the EMG signal was simultaneously monitored (Figure 7.17c and Figure 7.18b). The frequency spectrum of the signal obtained using nanopile electrode showed that the energy mainly concentrated in the frequency range of a few hundred Hertz (Figure 7.17 and Figure 7.16b) which is the typical distribution of EMG. However, the crack-based electrode showed much lower signal-noise-ratio (SNR) and it was hard to distinguish the EMG signal from the noise (Figure 7.17e,f). Additionally, the EMG signal was also measured by using

normal commercial non-stretchable electrodes that had no resistance change during the detection (Figure 7.18c). It shows that these electrodes have comparable signal-to-noise ratio (Figure 7.18d) indicating that the resistance change in the stretchable electrode has little effect on the accurate measurement (See more detailed discussion in the Supplemental Note and Figure 7.19-7.21).

Figure 7.17 Demonstration of the novel stretchable electrode and strain sensor detecting EMG signal and deformation induced by the elbow bending. a) Image illustrating the position of the fabricated stretchable electrodes and stretchable strain sensors and testing motion. b) Images of nanopile (left) and normal crack-based stretchable electrodes (right) after friction test. Red dashed boxes show the test region and the optical images present the corresponding magnified tested regions. c) EMG signal detected by the electrode with nanopiles after cyclic friction test. d) Energy spectrum analysis of the EMG signal showing the frequency range of main energy distribution. e) EMG signal detected by the CSGF after cyclic friction test. f) Signal-to-noise-ratio (SNR) comparison of those two electrodes.

Figure 7.18 The electrode can also be used as the stretchable strain sensor to detect the elbow bending in a), and the EMG signal by using the electrode before friction test is shown in b). c) EMG signal detected by commercial non-stretchable electrodes. d) Signal-to-noise ratio comparison between the nanopile stretchable electrode and the non-stretchable commercial electrode

Herein, in order to test how much strain will be induced, a marker of a red line was made on the volunteer's skin of biceps (with the same orientation with the electrode; see inset of Figure 7.18b) and measured the length change of this marker before and after muscle contraction (Figure 7.19a,b). The strain induced can be calculated as $(8.2-7.5) / 7.5$ (mm) $\sim 9.33\%$.

Figure 7.19 A marker of red line on the biceps was used to demonstrate the strain in the skin for relaxing state in a) and contraction in b). The length change reflected the strain of the skin. c) The resistance change of the stretchable electrode during the motion.

For the same procedure of the contraction and release of the biceps, how much strain was transferred from the skin to the electrode was also investigated by testing the resistance change of the stretchable electrode (Figure 7.19c). The resistance changed from ~ 7.5 ohm to ~ 9.5 ohm. The baseline is not at ~ 5.5 ohm as tested in Figure 3f. It is because there will be definitely pre-strain in the film during the processing of the electrode onto the skin. Thus, the total strain in the electrode, $\epsilon_t = \epsilon_{pre} + \epsilon_s$, where ϵ_{pre} is the pre-strain and ϵ_s is the strain induced by the skin deformation. Since the electrode has linear response to the strain, so $\epsilon_{pre} \sim (7.5-5.5) / (12.5-5.5) * 10\% \sim 2.86\%$ and $\epsilon_s \sim (9.5-7.5) / (12.5-5.5) * 10\% \sim 2.86\%$. And $\epsilon_t \sim 5.72\%$.

In addition, it should be notified that there was strain mismatch between the skin ($\sim 9.33\%$) and corresponding strain in the electrode ($\sim 2.86\%$). It was due to the Young's modulus difference. Normally, that of skin is ~ 100 kPa (refer to IEEE Trans Biomed Eng. 2010, 57, 953) and PDMS is ~ 1.8 MPa.

Figure 7.20 The FEM simulation to calculate the strain transferred from the skin to the electrode.

In order to further verify the test, finite element modeling (FEM) mechanical simulation was conducted to calculate the strain in the electrode by using software *Abaqus*. For this simulation, 3D modeling was employed with mesh type of C3D8R taking PDMS as elastic polymer and used 'Tie' interaction to combine the skin and the electrode assuming that the electrode was well adhered onto the skin and since the gold film is thin enough compared to the thickness of the PDMS substrate, its mechanical effect was ignored. Also, part of the electrode was only simulated and did not have to consider the effect of

the curvature of the skin. The calculation was performed at the workstation of Dell Precision T7610. The result showed that the strain in PDMS was around 2.466% when 9.33% strain was applied in the skin (Figure 7.20a). It was comparable with the tested strain ($\sim 2.86\%$) further proving that the testing was correct. It was also calculated the strain in the electrode with different strain in the skin, showing that the strain will not exceed 15% when it reached to 30% in the skin (Figure 7.20b).

Then three experimental evidence were provided to show that the DC resistance change in the electrode, i.e. the gauge factor, will not affect the accurate measurement of EMG signal.

From the perspective of the electrode characterization:

1. The strain in the electrode induced by the contraction of the biceps has already been evaluated. The $\sim 5.72\%$ strain did not affect the DC resistance significantly (from ~ 5.5 ohm to ~ 9.5 ohm). Compared with the impedance (~ 1300 ohm) of the electrode, only 0.3% variation was induced by the DC resistance. This fluctuation was much lower than that induced by the skin treatment, sweating, or mechanical slip (refer to “Surface Electromyography: Physiology, Engineering and Applications” 2016, Eds: Roberto Merletti, Dario Farina, Ch 3, pp 63-64). It had little effect on the accurate measurement.

In addition, even for the maximum strain in the skin ($\sim 30\%$), i.e., the strain in the electrode $< 15\%$, according to the gauge factor of 12.5, DC resistance change in the electrode $< 12.5 * 0.15 * 5.5 / 1300 \sim 0.8\%$.

From the perspective of the measured EMG signal:

1. Stretchable electrodes were fixed onto the rigid backing by using epoxy resin to make non-stretchable electrodes which will have negligible resistance change during the test. The whole electrode was sucked into the epoxy resin only exposing the gold film to detect the EMG signal (Figure 7.21a). The detected signal with amplitude spectrum analysis is shown in Figure 7.21b,c. It can be clearly seen that the spectrum of fixed electrode (Figure 7.21c) and free stretchable one (Figure 7.16b) has the similar feather of the energy distribution with respect to the frequency. The energy also concentrated below 1k Hz. Also, they had comparable signal-to-noise ratio (SNR) indicating that the DC resistance

change of the free stretchable electrode, i.e., the gauge factor, did not affect the accurate measurement (Figure 7.21d).

2. As responded before, the similar SNR of the signal detected by the commercial non-stretchable electrode with ours also indicated that it will not affect the accurate measurement.

Figure 7.21 The stretchable was sucked into the epoxy resin to become a non-stretchable electrode as the control. a) Image of the electrode. b) A typical EMG signal detected by this electrode. c) Amplitude spectrum analysis of the signal. d) SNR comparison of the free stretchable electrode and the fixed one

7.4 Conclusions

In summary, a new strategy, nanopile interlocking, was reported to obtain films possessing simultaneously high stretchability and strong adhesion by addressing the critical issues of adhesion governed by the intrinsic difference of the physical and chemical properties of metal and polymer. Films with an interpenetrating nanopile later display an interlocking effect with the elastic substrate that significantly increases the adhesion. It also adjusts the strain distribution in the metal film. The fabricated stretchable conductive metal film can be used both for stretchable electrodes and strain

sensors to reliably detect EMG signals and the joint motions. This study opens up a new perspective of simultaneously achieving films with high adhesion and large stretchability. Following this new routine and the strategy, many other methods could be proposed to develop highly stable stretchable electronic devices.

References:

- [1] S. Choi, H. Lee, R. Ghaffari, T. Hyeon, D. H. Kim, *Adv. Mater.* 2016, 28, 4203.
- [2] J. Liang, L. Li, D. Chen, T. Hajagos, Z. Ren, S.-Y. Chou, W. Hu, Q. Pei, *Nat. Commun.* 2015, 6, 7647.
- [3] S.-K. Kang, R.K.J. Murphy, S.-W. Hwang, S.M. Lee, D.V. Harburg, N.A. Krueger, J. Shin, P. gamble, H. Cheng, S. Yu, Z. Liu, J.G. McCall, M. Stephens, H. Ying, J. Kim, G. Park, R.C. Webb, C.H. Lee, S. Chung, D.S. Wie, A.D. Gujar, B. Vemulapalli, A.H. Kim, K-M. Lee, J. Cheng, Y. Huang, P.V. Braun, W.Z. Ray and J.A. Rogers, *Nature*, 2016, 530, 71.
- [4] B. C.-K. Tee and A. Chortos and A. Berndt, A. K. Nguyen, A. Tom, A. McGuire, Z. C. Lin, K. Tien, W.-G. Bae, H. Wang, P. Mei, H.-H. Chou, B. Cui, K. Deisseroth, T. N. Ng, Z. Bao, *Science*, 2015, 350, 313.
- [5] J. Liu, T.-M. Fu, Z. Cheng, G. Hong, T. Zhou, L. Jin, M. Duvvuri, Z. Jiang, P. Kruskal, C. Xie, *Nat. Nanotech.* 2015, 10, 629.
- [6] N. G. Tsagarakis, D. G. Caldwell, *Auton. Robots* 2003, 15, 21.
- [7] S. Lim, D. Son, J. Kim, Y. B. Lee, J. K. Song, S. Choi, D. J. Lee, J. H. Kim, M. Lee, T. Hyeon, D. H. Kim, *Adv. Funct. Mater.* 2015, 25, 375.
- [8] S. Jung, J. H. Kim, J. Kim, S. Choi, J. Lee, I. Park, T. Hyeon, D. H. Kim, *Adv. Mater.* 2014, 26, 4825.
- [9] J. W. Jeong, W. H. Yeo, A. Akhtar, J. J. Norton, Y. J. Kwack, S. Li, S. Y. Jung, Y. Su, W. Lee, J. Xia, H. Cheng, Y. Huang, W.-S. Choi, T. Bretl, J.A. Rogers, *Adv. Mater.* 2013, 25, 6839.
- [10] D.-H. Kim, R. Ghaffari, N. Lu, J. A. Rogers, *Annu. Rev. Biomed. Eng.* 2012, 14, 113.
- [11] I. R. Mineev, P. Musienko, A. Hirsch, Q. Barraud, N. Wenger, E. M. Moraud, J.

- Gandar, M. Capogrosso, T. Milekovic, L. Asboth, R. F. Torres, N. Vachicouras, Q. Liu, N. Pavlova, S. Duis, A. Larmagnac, J. Vörös, S. Micera, Z. Suo, G. Courtine, S. P. Lacour, *Science*, 2015, 347, 159.
- [12] S. P. Lee, L. E. Klinker, L. Ptaszek, J. Work, C. Liu, F. Quivara, C. Webb, C. Dagdeviren, J. A. Wright, J. N. Ruskin, M. Slepian, Y. Huang, M. Mansour, J. A. Rogers, R. Ghaffari, *Proc. IEEE* 2015, 103, 682.
- [13] D. Qi, Z. Liu, M. Yu, Y. Liu, Y. Tang, J. Lv, Y. Li, J. Wei, B. Liedberg, Z. Yu, X. Chen, *Adv. Mater.* 2015, 27, 3145.
- [14] T. Cheng, Y. Zhang, W. Y. Lai, W. Huang, *Adv. Mater.* 2015, 27, 3349.
- [15] C. Guo, Y. Chen, L. Tang, F. Wang, Z. Ren, *Nano Lett.* 2016, 16, 594.
- [16] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J.-H. Ahn, P. Kim, J.-Y. Choi, B. H. Hong, *Nature*, 2009, 457, 706.
- [17] M.-S. Lee, K. Lee, S.-Y. Kim, H. Lee, J. Park, K.-H. Choi, H.-K. Kim, D.-G. Kim, D.-Y. Lee, S. Nam, J. U. Park, *Nano Lett.* 2013, 13, 2814.
- [18] C. Keplinger, J.-Y. Sun, C. C. Foo, P. Rothemund, G. M. Whitesides, Z. Suo, *Science* 2013, 341, 984.
- [19] T. Yamada, Y. Hayamizu, Y. Yamamoto, Y. Yomogida, A. Izadi-Najafabadi, D. N. Futaba, K. Hata, *Nat. Nanotech.* 2011, 6, 296.
- [20] X. Li, R. Zhang, W. Yu, K. Wang, J. Wei, D. Wu, A. Cao, Z. Li, Y. Cheng, Q. Zheng, *Sci. Rep.* 2012, 2, 870.
- [21] J. T. Muth, D. M. Vogt, R. L. Truby, Y. Mengüç, D. B. Kolesky, R. J. Wood, J. A. Lewis, *Adv. Mater.* 2014, 26, 6307.
- [22] B. Sun, Y.-Z. Long, S.-L. Liu, Y.-Y. Huang, J. Ma, H.-D. Zhang, G. Shen, S. Xu, *Nanoscale* 2013, 5, 7041.
- [23] X. Xiao, L. Yuan, J. Zhong, T. Ding, Y. Liu, Z. Cai, Y. Rong, H. Han, J. Zhou, Z. L. Wang, *Adv. Mater.* 2011, 23, 5440.
- [24] C. Yan, J. Wang, W. Kang, M. Cui, X. Wang, C. Y. Foo, K. J. Chee, P. S. Lee, *Adv. Mater.* 2014, 26, 2022.
- [25] X. Wang, Y. Gu, Z. Xiong, Z. Cui, T. Zhang, *Adv. Mater.* 2014, 26, 1336.
- [26] K.-I. Jang, S. Y. Han, S. Xu, K. E. Mathewson, Y. Zhang, J.-W. Jeong, G.-T. Kim, R. C. Webb, J. W. Lee, T. J. Dawidczyk, R.H. Kim, Y.M. Song, W.-H. Yeo, S. Kim, H.Y. Cheng, S.I. Rhee, J.H. Chung, B.G. Kim, H.U. Chung, D.J. Lee, Y.Y. Yang,

- M.G. Cho, J.G. Gaspar, R. Carbonari, M. Fabiani, G. Gratton, Y.G. Huang and J.A. Rogers, *Nat. Commun.* 2014, 5, 4779.
- [27] J. J. Park, W. J. Hyun, S. C. Mun, Y. T. Park, O. O. Park, *ACS Appl. Mater. Interfaces* 2015, 7, 6317.
- [28] X. Zhao, Q. Hua, R. Yu, Y. Zhang, C. Pan, *Adv. Electron. Mater.* 2015, 1500142.
- [29] M. Kubo, X. Li, C. Kim, M. Hashimoto, B. J. Wiley, D. Ham, G. M. Whitesides, *Adv. Mater.* 2010, 22, 2749.
- [30] L. Song, A. C. Myers, J. J. Adams, Y. Zhu, *ACS Appl. Mater. Interfaces* 2014, 6, 4248.
- [31] D. S. Gray, J. Tien, C. S. Chen, *Adv. Mater.* 2004, 16, 393.
- [32] S. Xu, Y. Zhang, J. Cho, J. Lee, X. Huang, L. Jia, J. A. Fan, Y. Su, J. Su, H. Zhang, *Nat. Commun.* 2013, 4, 1543.
- [33] C. F. Guo, T. Sun, Q. Liu, Z. Suo, Z. Ren, *Nat. Commun.* 2014, 5, 3121.
- [34] J. Mertens, R. W. Bowman, J. C. Willis, A. Robinson, D. Cotton, R. White, K. A. Seffen, J. J. Baumberg, *Phy. Rev. Appl.* 2015, 4, 044006.
- [35] F. Xu, Y. Zhu, *Adv. Mater.* 2012, 24, 5117.
- [36] Z. Niu, H. Dong, B. Zhu, J. Li, H. H. Hng, W. Zhou, X. Chen, S. Xie, *Adv. Mater.* 2013, 25, 1058.
- [37] M. Park, J. Im, M. Shin, Y. Min, J. Park, H. Cho, S. Park, M.-B. Shim, S. Jeon, D.-Y. Chung, J. Bae, J. Park, U. Jeong, K. Kim, *Nat. Nanotech.* 2012, 7, 803.
- [38] M. Park, J. Park, U. Jeong, *Nano Today* 2014, 9, 244.
- [39] C. L. Choong, M. B. Shim, B. S. Lee, S. Jeon, D. S. Ko, T. H. Kang, J. Bae, S. H. Lee, K. E. Byun, J. Im, Y. Jeong, C. Park, J.-J. Park, U.-I. Chung, *Adv. Mater.* 2014, 26, 3451.
- [40] M. Chen, T. Tao, L. Zhang, W. Gao, C. Li, *Chem. Commun.* 2013, 49, 1612.
- [41] J. Yoon, S. Y. Hong, Y. Lim, S. J. Lee, G. Zi, J. S. Ha, *Adv. Mater.* 2014, 26, 6580.
- [42] J. W. Boley, E. L. White, G. T. C. Chiu, R. K. Kramer, *Adv. Funct. Mater.* 2014, 24, 3501.
- [43] J. Y. Sun, C. Keplinger, G. M. Whitesides, Z. Suo, *Adv. Mater.* 2014, 26, 7608.
- [44] Z. Liu, M. Yu, J. Lv, Y. Li, Z. Yu, *ACS Appl. Mater. Interfaces* 2014, 6, 13487.
- [45] Z. Liu, D. Qi, P. Guo, Y. Liu, B. Zhu, H. Yang, Y. Liu, B. Li, C. Zhang, J. Yu, *Adv. Mater.* 2015, 27, 6230.

- [46] S. P. Lacour, J. Jones, S. Wagner, T. Li, Z. Suo, *Proc. IEEE* 2005, 93, 1459.
- [47] A. Chortos, J. Lim, J. W. To, M. Vosgueritchian, T. J. Dusseault, T. H. Kim, S. Hwang, Z. Bao, *Adv. Mater.* 2014, 26, 4253.
- [48] H. Vandeparre, Q. Liu, I. R. Mineev, Z. Suo, S. P. Lacour, *Adv. Mater.* 2013, 25, 3117.
- [49] H. L. Filiatrault, R. S. Carmichael, R. A. Boutette, T. B. Carmichael, *ACS Appl. Mater. Interfaces* 2015, 7, 20745.
- [50] O. Akogwu, D. Kwabi, A. Munhutu, T. Tong, W. Soboyejo, *J. Appl. Phys.* 2010, 108, 123509.
- [51] O. Van Der Sluis, Y.-Y. Hsu, P. Timmermans, M. Gonzalez, J. Hoefnagels, *J. Phys. D: Appl. Phys.* 2010, 44, 034008.
- [52] Y. Huang, Y. Huang, W. Meng, M. Zhu, H. Xue, C.-S. Lee, C. Zhi, *ACS Appl. Mater. Interfaces* 2015, 7, 2569.
- [53] J. Hoefnagels, J. Neggers, P. Timmermans, O. van der Sluis, M. Geers, *Scr. Mater.* 2010, 63, 875.
- [54] T. Li, Z. Suo, S. P. Lacour, S. Wagner, *J. Mater. Res.* 2005, 20, 3274.
- [55] D. Vella, J. Bico, A. Boudaoud, B. Roman, P. M. Reis, *Proc. Natl. Acad. Sci.* 2009, 106, 10901.
- [56] B. G. Vossen, P. J. Schreurs, O. van der Sluis, M. Geers, *J. Mech. Phys. Solids* 2014, 66, 117.
- [57] Y.-Y. Hsu, C. Papakyrikos, D. Liu, X. Wang, M. Raj, B. Zhang, R. Ghaffari, *J. Micromech. Microeng.* 2014, 24, 095014.
- [58] Y.-Y. Hsu, M. Gonzalez, F. Bossuyt, F. Axisa, J. Vanfleteren, I. De Wolf, *J. Micromech. Microeng.* 2010, 20, 075036.
- [59] J. Tang, J. Li, J. J. Vlassak, Z. Suo, *Soft Matter*. 2016, 12, 1093.
- [60] M. Gonzalez, F. Axisa, M. V. Bulcke, D. Brosteaux, B. Vandeveld, J. Vanfleteren, *Microelectronics Reliab.* 2008, 48, 825.
- [61] D. J. Lipomi, *Adv. Mater.* 2016, 28, 4180.
- [62] P. Schupbach, R. Glauser, *J. Prosthet. Dent.* 2007, 97, S15.
- [63] J. Subbaroyan, D. C. Martin, D. R. Kipke, *J. Neural Eng.* 2005, 2, 103.
- [64] R. C. Webb, A. P. Bonifas, A. Behnaz, Y. Zhang, K. J. Yu, H. Cheng, M. Shi, Z. Bian, Z. Liu, Y.-S. Kim, W.-H. Yeo, J. S. Park, J. Song, Y. Li, Y. Huang, A. M. Gorbach, J. A. Rogers, *Nat. Mater.* 2013, 12, 938.

- [65]S. J. Hurst, E. K. Payne, L. Qin, C. A. Mirkin, *Angew. Chem. Int. Ed.* 2006, 45, 2672.
- [66]F. Meng, Y.-M. Hervault, Q. Shao, B. Hu, L. Norel, S. Rigaut, X. Chen, *Nat. Commun.* 2014, 5, 3023.
- [67]O. Graudejus, P. Görrn, S. Wagner, *ACS Appl. Mater. Interfaces* 2010, 2, 1927.
- [68]C. R. C. Lima, J. M. Guilemany, *Surf. Coat Technol.* 2007, 201, 4694.
- [69]P. Chalker, S. Bull, D. Rickerby, *Mater. Sci. Eng. A* 1991, 140, 583.
- [70]Y. H. Yin, Y. J. Fan, L. D. Xu, *IEEE Trans. Inf. Technol. Biomed.* 2012, 16, 542.
- [71]K. Kiguchi, T. Tanaka, T. Fukuda, *IEEE Trans. Fuzzy Syst.* 2004, 12, 481.
- [72]A. Gruebler, K. Suzuki, *IEEE Trans. Affect. Comput.* 2014, 5, 227.
- [73]H. Zhivomirov, Sound analysis with Matlab Implementation, <http://www.mathworks.com/matlabcentral/fileexchange/38837-sound-analysis-with-matlab-implementation>, accessed: April 2014.

Chapter 8

Synchronous Interface Forming of Metal Film and Polymer for High-performance Stretchable Conductors*

A new strategy, dynamic interface mingling of elastic polymer and metal, is reported to fabricate stretchable conductors with high stretchability and stability, high surface area and most importantly, high adhesion between the metal, gold, and elastic polymer, Polydimethylsiloxane (PDMS). The underlying knack is to use uncured PDMS instead of fully cured one to receive the gold atoms generated by the thermal evaporation. It will trigger a series of dynamic chemical and physical processes fabricating stretchable conductors with the unique microstructure of self-stripped kalst caves-like double layers and the superior performance.

*To be published substantially as Liu et al., Dynamic interface mingling for high-performance stretchable electrodes.

8.1 Introduction

Recent years witness the paradigm shift in the research field from silicon-based rigid electronics to bio-materials/elastic materials-based deformable electronics.^[1-7] The underlying driven force is the pursuing for more human-friendly electronics and even the human-machine integration to further facilitate daily life and enhance human power. Under this direction, soft implantable devices,^[8, 9] flexible electronic interfaces,^[10, 11] smart sensors for Internet of Things (IoT),^[12-14] wearable diagnosis sensors,^[15-17] flexible batteries,^[18-20] soft robotics,^[21-23] and other stretchable devices are all in the rapid development.^[24-32]

For all of these flexible/stretchable devices, stretchable conductors, which can keep conductive under large mechanical deformation ($> 30\%$ strain), are the most fundamental units to achieve desired functions.^[33] However, naturally, there are hardly intrinsically stretchable fully conductive materials. Several strategies were proposed to fabricate the stretchable fully conductive materials by combining the elastic polymer with fully conductive materials, such as metal and carbon.^[34-58] Nevertheless, poor interfacial adhesion was also induced by this direct combination, especially for the conductive metal film on elastic substrate, because of the totally different physical and chemical properties of organic polymer and inorganic conductive materials.^[59-61] Adhesion is vital both for the subsequent conductor encapsulation process which typically involves the multi-mask photolithography or the peel-off process demanding good adhesion of the metal film on elastic substrate, and for the practical use, such as interface signal monitoring which inevitably involves the severe interface friction. If metal film could not well adhere to the elastic substrate, the stretchable conductor either can not go through the encapsulation process or fails in the short term in practical applications. So how to achieve high adhesion and high stretchability simultaneously is a big challenge for the reliable stretchable electronics.

Herein, a new strategy, dynamic interface mingling of elastic polymer and metal, is reported to fabricate stretchable conductors with high stretchability and stability, high surface area and most importantly, high adhesion between the metal, gold, and elastic polymer, Polydimethylsiloxane (PDMS). The underlying knack is to use uncured PDMS

instead of fully cured one to receive the gold atoms generated by the thermal evaporation. It will trigger a series of dynamic chemical and physical processes fabricating stretchable conductors with the unique microstructure of self-stripped kalst caves-like double layers and the superior performance. The stretchability ($> 130\%$) was achieved by the strain redistribution by the tuning effect of the micro pillars inbetween the stripped gold-PDMS mingling layer and the PDMS substrate. High adhesion ($> 2 \text{ MPa}$) was achieved because of the mingling effect at the interface. The film can be fabricated in large scale easily ($> 10 \text{ cm} \times 10 \text{ cm}$). Both stretchability and good adhesion are essential for the implantation electrode because of the inevitable friction between the tissue and electrode. As a proof of concept, the novel stretchable electrodes were implanted and entwined around the sciatic nerve in rats as neural stimulators. The induced myoelectricity signal was recorded accordingly. Our novel strategy, dynamic interface mingling, is easy-to-use and opens a new path to achieve stretchability and high adhesion simultaneously. The obtained high-performance stretchable conductors take a solid step towards the practical application of stretchable electronics.

8.2 Experimental Methods

8.2.1 Half-cured PDMS preparation

Glass slides without any pre-treatment worked as the rigid backing for uncured PDMS (184, Dow Corning) with different ratio of cross linker to monomer of 1:5, 1:10, 1:20 and different pre-curing time of 15, 20, 25 minutes, respectively, in the 60°C oven. The sample was pasted onto the trial of the thermal evaporation machine with the PDMS film facing down towards the gold source.

8.2.2 Thermal evaporation of gold film and other testing

When the vacuum achieved to 1.0×10^{-6} Torr, the chromium and gold source was heated up and started to evaporate in sequence at the rate of 0.2 and $0.5 \text{ \AA s}^{-1}$, respectively. The sample was ready after the evaporation.

Preparation of normal stretchable and flat non-stretchable gold film: As control samples, films were prepared following the previous method.^[68] The normal crack-based

stretchable gold film had an appearance of brown color due to the thin film thickness required by the special morphology of initial nano cracks. The thickness of the film was around 80 nm. The up limit of the thickness for this stretchable film was around 100 nm.

Peel test of tensile adhesion strength: The strength was obtained following the classical test process. The cylindrical wood sticks were well adhered to samples by epoxy resin. MTS C42 with 50 N load cell was employed to test the adhesion force when the stick was pulled up by the Bionix vice grips. Moreover, the synchronous measurement of resistance and tensile strain was performed as reported previously.^[69]

Animal surgery and neural stimulation: Adult male Sprague-Dawley rats (150 – 200g) were obtained from Guangdong Medical Experimental Animal Center (Guangdong, China). All procedures were carried out under the guidelines of the Institutional Animal Care and Use Committee of Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences. The anesthesia and surgery followed the standard procedures. The electrode was carefully implanted and entwined around the sciatic nerve and did the stimulation and EMG recording by using Medlab biological signal collecting and handling system.

8.3 Principal Outcomes

8.3.1 Large-scale high-performance stretchable electrodes

Normally, PDMS is always used after being fully cured and then undergoes the subsequent fabrication process, for example deposited with metal/semiconductor film after certain pre-treatment (like oxygen plasma).^[56, 62] The concept is that why not deposit metal film when the polymer is in partially cured state (Figure 8.1a), which would induce a series of dynamic physical-chemical process, and most importantly, the evaporated metal would mingle with the elastic substrate. Thus, metal and polymer could enter into each other at the interface that could result in high adhesion between them.

Figure 8.1 Schematic diagram of the strategy of dynamic interface mingling and corresponding physical analyses. a) Diagram illustrating to show the fabrication process and uncured PDMS was used as the substrate to receive the evaporated gold. b) Physical models of heat transfer and viscous flow during the dynamic process. c) Simulation results of the temperature distribution in the film and corresponding pressure distribution during the viscous flow under different viscosity (low viscosity in left and higher in right). d) Diagram of the unique self-stripping double-layer structure.

Detailed physical-chemical processes could be predicted as follows (they all happen simultaneously) (Figure 8.1b): 1. PDMS and gold mingle together and enter into each other at the interface, when the hot fast-speed gold strikes onto the soft uncured PDMS. 2. During Step 1, partially cured PDMS still undergoes the polymerization and does much faster under the thermal radiation of the gold source (temperature can be up to 1800 K) and heat transfer from the hot deposited gold. The quasi-steady-state heat transfer for certain unit of the film includes the processes of heat input from the thermal radiation and the hot deposited gold, Q_I , and heat dissipation from the thermal radiation at both sides of the film, Q_{d1} and Q_{d2} , and conduction at the backing, Q_{d3} (heat convection can be

omitted). Under the hypothesis of quasi-steady state, $Q_I \approx Q_{d1} + Q_{d2} + Q_{d3}$ (Figure 1b). Then the temperature distribution can be roughly obtained (Figure 1c).

Figure 8.2 Structures of the film with and without strain applied. a,b) Cross-section SEM images of the self-stripping double-layer structure. Insets in a) show optical images of the front and reverse views of the sample with large area. The reverse is in black color resulted from the absorption effect by the gold nanoparticles and PDMS mingling layer. c,d) SEM and AFM images of the gold film showing the wrinkled structure with upheaval and depression. e) SEM image of the stretchable film under tensile strain of 50 %. Inset shows connecting bridge by the upheaval twisting. f) Resistance change under the tensile strain and it is out of the measurement range at around 135%. Inset presents the optical image of the testing process.

Because of the low thermal conductivity of PDMS and relatively slow thermal dissipation rate, the temperature gradient exists inside the film. The maximum temperature can be $\sim 120\text{ }^{\circ}\text{C}$ that significantly speeds up the polymerization of the bottom. It's worth also emphasising that the temperature of the bottom near to the heat source could be higher than $120\text{ }^{\circ}\text{C}$ when the thermal diffusion is not in steady state actually. 3. During Step 1 and 2, mechanical process happens simultaneously (Figure 8.1b). Density of gold ($19,300\text{ kg m}^{-3}$) is much higher than that of PDMS (0.97 kg m^{-3}). With the increase of the deposition of gold at the interface, gold would pull down one thin layer of PDMS. However, at the same time, partially cured PDMS becomes high-viscosity rapidly when the temperature goes up as discussed in Step 2. Eventually, the self-weight, G , balances with the viscosity force of PDMS, F_{η} , and the viscous film would not move downward once the viscosity is large enough as proven by the simulation (Figure 8.1c), which means that the film shape will be rapidly frozen due to the temperature rising.

Figure 8.3 SEM images to further investigate the cross-section and surface structures. a,b) SEM images of the cross-section view. c,d) Detailed surface morphology of the conductor.

Finally, since the thermal evaporation rate is slow (usually $\sim 0.5\text{ \AA s}^{-1}$) and it takes around 33 minutes to deposit a 100 nm-thickness film, the whole elastic substrate is fully

polymerized during this process. Thus, the obtained film should possess a special structure: suspended layered composite one with mingling effect at the interface supported by pulled-out micro pillars during above dynamic processes (Figure 8.1d). It is proven subsequently that this special structure could endow the film with high stretchability, stability, high adhesion and high surface area. The strategy proposed here breaks the routine and opens up a new perspective to fabricate stretchable conductors. Considering the simple fabrication process and large-scale yield (inset of Figure 8.2a), the novel high-performance film would be one of the best candidates for stretchable electrodes, soft sensors and other flexible electronics in the real application.

Figure 8.4 Different wrinkled structure with different ratio and pre-curing time. a-c) Different pre-curing time with the ratio of cross linker to monomer of 1:10. and for 1:20 in d-f).

From the cross-section field emission scanning electron microscope (FESEM) image, the beautiful karst caves-like composite structure can be clearly observed (Figure 8.2a,b and 8.3). The suspended film was with two layers of gold and PDMS and the transitional layer between them induced by the mingling effect can also be roughly observed (Figure 8.3a,b). It was linked with the substrate by micro pillars underneath. Also, the surface morphology of the film was in random wrinkled state (Figure 8.2c,d), which should be induced by the modulus mismatch between the gold and PDMS during the dynamic polymerization. When investigated in detail, the wrinkled film was consisted of gold nanoparticles (grain size is ~ 20 nm) (Figure 8.3c,d). We also studied the effect of weight

ratio of cross linker to PDMS monomer and the pre-cured time on the surface morphology and subsequent performance. Different wrinkled structures can be obtained with different fabrication conditions (Figure 8.4a-f). When the pre-cure time was the same, the wrinkles became denser for lower ratio and the amplitude was smaller (Figure 8.5a-f).

Figure 8.5 Amplitude comparison of the wrinkle. a-c) AFM image and the section amplitude data shown in c). The film thickness is 300 nm (1:10, 25 mins). d,e) AFM image and the data for the same thickness film (1:20, 25mins). f) The amplitude comparison of the above two film.

8.3.2 Principle of the stretchability achieved

Figure 8.6 Comparison of the wrinkles structures of the novel stretchable conductor and that fabricated by the traditional pre-biaxial strain method. a,b) Diagram to present the fabrication process of the pre-biaxial strain method. c) Typical wrinkled structure of the novel conductor for relatively thick gold film (200 nm). d) SEM image to present the surface morphology of the traditional film with the same film thickness.

It should be emphasized that wrinkles here are different with that fabricated by the normal pre-stretch method.^[63-65] The latter actually requires relatively smaller thickness of the metal film on top. In order to get the similar pattern, 2D pre-strain should be applied inside the elastic substrate (Figure 8.6a,b) and then deposited with metal film. When released, 2D pattern appeared due to the mismatch of the modulus. However, the amplitude of those wrinkles was highly dependent on the adhesion and the thickness of the metal film. If the thickness is too large (like ~ 300 nm), it is hard to form regular dense wrinkle structure according to the buckling theory.^[63] The experiment also proved that there were hardly wrinkles for the gold film (Figure 8.6c,d). Wrinkles still exist for the gold film thickness of as large as 500 nm by using the novel method due to the good adhesion and the special dynamic mingling process (Figure 8.7a,b). The wrinkle structure also contributed to the stretchability of the film. During the stretch, initial cracks appeared at the depression positions (Figure 8.2e) and then propagated. Some upheaval blocks twisted and still kept connected (inset of Figure 8.2e, and Figure 8.8 a,b).

However, obviously, not all upheaval blocks connected in the cracks. Besides, the stretchability achieved by the novel films was surprisingly good ($> 130\%$) (Figure 8.2f). There must be another dominated mechanism behind. Observed closely, the stretchable film showed numerous random distributed micro cracks (Figure 8.2e and Figure 8.8c-f), indicating that the strain energy was released by those micro cracks forming connecting network inside the film. The strain regulation effect induced by micro pillars underneath is crucial. this effect was simulated by placing random micro pillars under the suspended film (Figure 8.7a) and the results showed that the strain distribution was indeed regulated by the pillars underneath to the relatively random style, compared to the flat film without micro pillars (Figure 8.7b and Figure 8.9). The strain distribution determined the crack formation during the stretch and random distribution significantly benefited the stretchability.

Figure 8.7 Mechanism of the stretchability and the performance of the stretchable conductor. a-b) Finite element method simulation results to present the strain redistribution mechanism behind the stretchability. c) Resistance change under cyclic tensile strain. d) Stretchability variation with different ratio of cross link to monomer and pre-curing time of PDMS. e) Stretchability and gauge factor affected by the gold film thickness. f) Adhesion with different ratio and pre-curing time. NCSG refers to normal crack-based stretchable gold film and FNSG refers to flat non-stretchable gold film.

Figure 8.8 SEM images of the stretchable conductor under tensile strain. a,b) The connecting effect by the twisting of the upheaval. c,d) The morphology of the film under 30% strain. The film is with cross linker to monomer ratio of 1:5 and pre-curing time of 25 mins, and the corresponding morphology for the film with 1:10 ratio and 25 mins pre-curing time is shown in e,f).

Those random distributed micro cracks will increase the resistance making the stretchable conductor as a stretchable strain sensor to detect the how large the mechanical deformation is applied in the film, and the sensitivity, reflected by the gauge factor defined as $\Delta R/R_0/\epsilon$, can achieve to as large as 20. The resistance change is quite repeatable at least for 1,000 strain cycles (Figure 8.7c). Moreover, the effect of the ratio of cross linker to monomer and pre-cured time on the stretchability and gauge factor was investigated in detail. The stretchability decreased with the decrease of the ratio and the

pre-curing time, indicating that the film possesses poor stretchability for initially less cured PDMS that is less viscous. The liquid with less viscosity tends to be discontinuous during the stretching, whereas the suspended composite film tended to dropdown more, i.e., more stretching, for less viscous liquid according to the simulation result of viscous flow (Figure 8.1c). So, the number of the pulled-out micro pillars will decrease dramatically for less-viscosity film in this process making it lose the ability of strain regulation and the strain tended to concentrate causing poor stretchability. It was also true for the situation that thin gold film was deposited, because the heat transfer became less for thinner film deposition which was equivalent to the less pre-curing. But when the film thickness was further increased, the wrinkle structure will be relatively filled up. Also, the larger thickness would increase the defects inside the film and lower the ductility of the film. So the stretchability decreased again with the further increase of the film thickness (Figure 8.7e). Additionally, since the sensitivity is the reverse behavior to the stretchability, it also showed reverse change trend with respect to the stretchability (Figure 8.7e).

Figure 8.9 FEM simulation model and results. a) Model of the substrate with randomly oriented micro pillars. b) The strain regulation effect induced by the micro pillars.

Figure 8.10 Adhesion comparison by using Kapton tape. a-c) The testing process for the flat non-stretchable gold film, and for normal crack-based stretchable gold film and the novel stretchable conductor in d-f) and g-i), respectively. j) The transient resistance measured by multi-meter to present the conductivity after the peel test in g-i).

The adhesion performance is vital for the real application of stretchable electronics. It was found that the adhesion strength achieved to as large as about 2 MPa that is much larger than that of normal crack-based stretchable gold film (NCSG) (~ 0.2 MPa) and the flat non-stretchable gold film (FNSG) (~ 0.5 MPa) (Both are with 10 nm Chromium as the adhesive layer) (Figure 8.7f). In order to intuitively demonstrate the adhesion enhancement, high-adhesion Kapton tape was employed to do the comparison peel test (Figure 8.10 and Video 2). It was clearly shown that the high-adhesion Kapton tape made little damage to the novel film, but peeled a large area of the film from the normal stretchable gold film and non-stretchable gold film. The good adhesion achieved was due to the dynamic mingling process as discussed before. The hot high-speed gold nanoparticles stroke into the un-cured polymer and fully inter-connected with the substrate (Figure 8.11).

Figure 8.11 Mingling effect of the evaporated gold and PDMS. a) SEM image to show the cross-section view of the gold film. b) The magnified view of mingling effect at the interface.

Figure 8.12 SEM images to show the fracture mechanism of the suspended film on PDMS substrate. a-b) Surface morphology of the bottom of the suspended film, indicating that the fracture point is near to the junction of the micro pillars and the film. c-d) The corresponding view of the morphology on PDMS substrate. Micro pillars are left on the substrate.

After the peel test, the surface morphology of both the top of the PDMS substrate and the

bottom of the suspended film were investigated in order to investigate the fracture mechanism. It was found that the micro pillar was broken at the junction between the pillar and the suspended film. The bottom of the gold film was exposed (Figure 8.12a,b), indicating that the fracture was still induced by the interface failure although the mingling effect already significantly enhanced the adhesion. The fracture strength of PDMS film under tensile strain is around 2.24 MPa,^[67] whereas the adhesion strength of the novel film can achieve to 2 MPa which is comparable with the fracture one, indicating that the achieved adhesion strength almost reached the limit. Correspondingly, the pillar was observed on the PDMS substrate (Figure 8.12c,d). This morphology also verified the successful fabrication of the unique suspended double-layer composite film in large area.

The novel stretchable conductors with high adhesion, which can be fabricated simply in large area, have huge potential in the practical application in the field of implantable soft electrodes, body-surface electrophysiology signal detection and other stretchable smart sensors.

8.3.3 Bio-electrical signal detections

As a proof of concept, it was demonstrate that the stretchable conductors can be utilized as neural stimulators to efficiently apply stimulation voltage driving the movement of thigh muscle of rats, indicating that they could be used as the neural stimulation electrode for neural regeneration and rehabilitation. Benefiting from the wrinkle structure, the electrode has larger equivalent surface area and lower impedance as a result. The impedance of the electrode was monitored and made the fitting model by employing the typical constant phase element to obtain the equivalent capacitance per area (Figure 8.13a). The interface capacitance was at least 4 times larger than that of the flat gold film. It was also tunable simply by using PDMS with different ratio of cross linker to monomer (Figure 8.13b) because of the different density of the wrinkles achieved as discussed before. Taking this advantage, the novel stretchable electrodes were implanted and entwined round the tracts of sciatic nerve in thigh muscle of rats as nerve stimulators, and monitored the induced EMG signal simultaneously (Figure 8.13c and Figure 8.14a). The sciatic nerve was successfully entwined and stimulated by soft electrodes (Figure 8.13d).

Both the stimulation and EMG detection was well applied and monitored with clear input and output signals (Figure 8.13e,f). The EMG response was more sensitive at the early stage of the stimulation and became less sensitive with the increase of the applied stimulation voltage in terms of the peak-peak value of the response (Figure 8.13b). With further surface modification and treatment, novel electrodes could be used as the long-term implantable ones to monitor/stimulate the target nerve, because of the superior performance on the stretchability, stability, biocompatibility, high surface area and high adhesion.

Figure 8.13 Demonstration of the novel stretchable conductor as the neural stimulator. a) Impedance of the electrode. Inset shows the fitting model to calculate the equivalent capacitance. b) Comparison of the equivalent capacitance of the wrinkled-surface novel conductor with the flat gold film. The capacitance is normalized by that of the flat gold film. c) Diagram of the set up to stimulate the sciatic nerve by stretchable conductor and EMG monitoring system. d) Optical image to present the implanted stretchable conductor. e,f) Stimulation signal applied and the corresponding induced EMG signal detected.

Figure 8.14 Demonstration of the stretchable conductor as the neural stimulator. a) Setup of the stimulation and EMG monitoring. b) Peak-peak value of the induced EMG signal with different stimulation voltage.

8.4 Conclusions

In summary, a new strategy, dynamic interface mingling, is reported to fabricate high-performance stretchable conductors. Opposite to the traditional fabrication method, uncured PDMS was used to accept the gold nanoparticles generated by the thermal evaporation. The evaporated gold mingled with PDMS dynamically at the interface. The three physical-chemical processes: mingling effect, PDMS polymerization under the heat radiation by the thermal evaporation and the energy carried by the evaporated gold, and the stripping of gold-PDMS ultrathin layer under the gravity, happened at the same time. The unique self-stripped kalst caves-like structure with wrinkled surface was fabricated in large area. It can redistribute the strain from the concentration mode of flat film to the relatively random mode, achieving the high stretchability. Mingling effect enhanced the adhesion significantly and wrinkles structure increased the surface area of the electrode. The stretchable conductor can be used to monitor the mechanical deformation and electrophysiology signals. It can also act as the implantable nerve stimulator as demonstrated to benefit the neural regeneration/rehabilitation. The high-performance stretchable conductors take a solid step toward the practical applications. And the novel strategy opens a new perspective to composite metal and polymer. Following it, many other stretchable composite films could be further developed.

References:

- [1] J. A. Rogers, T. Someya, Y. Huang, *Science* 2010, 327, 1603.
- [2] S. Choi, H. Lee, R. Ghaffari, T. Hyeon, D. H. Kim, *Adv. Mater.* 2016, 28, 4203.
- [3] M. Park, J. Park, U. Jeong, *Nano Today* 2014, 9, 244.
- [4] S. Bauer, I. Graz, M. Kaltenbrunner, C. Keplinger, R. Schwödiauer, *Adv. Mater.* 2014, 26, 149.
- [5] S. Lin, H. Yuk, T. Zhang, G. A. Parada, H. Koo, C. Yu, X. Zhao, *Adv. Mater.* 2015, 28, 4497.
- [6] A. Chortos, G. I. Koleilat, R. Pfattner, D. Kong, P. Lin, R. Nur, T. Lei, H. Wang, N. Liu, Y. C. Lai, *Adv. Mater.* 2015, 28, 4441.
- [7] Z. Bao, X. Chen, *Adv. Mater.* 2016, 28, 4177.
- [8] S. I. Park, D. S. Brenner, G. Shin, C. D. Morgan, B. A. Copits, H. U. Chung, M. Y. Pullen, K. N. Noh, S. Davidson, S. J. Oh, *Nat. Biotechnol.* 2015, 33, 1280.
- [9] J. H. Lee, H. Kim, J. H. Kim, S.-H. Lee, *Lab Chip* 2016, 16, 959.
- [10] S. Lim, D. Son, J. Kim, Y. B. Lee, J. K. Song, S. Choi, D. J. Lee, J. H. Kim, M. Lee, T. Hyeon, *Adv. Funct. Mater.* 2015, 25, 375.
- [11] L. Guo, M. Ma, N. Zhang, R. Langer, D. G. Anderson, *Adv. Mater.* 2014, 26, 1427.
- [12] Y. Arafat, I. Dutta, R. Panat, *Appl. Phys. Lett.* 2015, 107, 081906.
- [13] A. M. Hussain, M. M. Hussain, *Adv. Mater.* 2015, 28, 4219.
- [14] H. M. Liu, G. Y. Yang, Q. Li, in *Advanced Materials Research*, Vol. 2 (Eds: X.S. George Zhao, H. Si and P. Xu), Trans. Tech. Publications, Germany 2014, Ch. 6.
- [15] L. Guan, A. Nilghaz, B. Su, L. Jiang, W. Cheng, W. Shen, *Adv. Funct. Mater.* 2016, doi: 10.1002/adfm.201600443.
- [16] S. J. Kim, K. W. Cho, H. R. Cho, L. Wang, S. Y. Park, S. E. Lee, T. Hyeon, N. Lu, S. H. Choi, D. H. Kim, *Adv. Funct. Mater.* 2016, 26, 3207.
- [17] S. Choi, J. Park, W. Hyun, J. Kim, J. Kim, Y. B. Lee, C. Song, H. J. Hwang, J. H. Kim, T. Hyeon, *ACS nano* 2015, 9, 6626.
- [18] J. Ren, Y. Zhang, W. Bai, X. Chen, Z. Zhang, X. Fang, W. Weng, Y. Wang, H. Peng, *Angew. Chem. Int. Edit* 2014, 126, 7998.
- [19] G. Kettlgruber, M. Kaltenbrunner, C. M. Siket, R. Moser, I. M. Graz, R. Schwödiauer, S. Bauer, *J. Mater. Chem. A* 2013, 1, 5505.

- [20] C. Yan, P. S. Lee, *Small* 2014, 10, 3443.
- [21] M. Vosgueritchian, J. B.-H. Tok, Z. Bao, *Nature Photonics* 2013, 7, 769.
- [22] J. O'Neill, J. Lu, R. Dockter, T. Kowalewski, in *International Conference on Robotics and Automation (ICRA)*, IEEE, 2015, pp 624.
- [23] S. Russo, T. Ranzani, H. Liu, S. Nefti-Meziani, K. Althoefer, A. Menciassi, *Soft Robotics* 2015, 2, 146.
- [24] W. H. Kang, W. Cao, S. Wagner, B. Morrison, in *Stretchable Electronics* (Ed: T. Someya), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany 2012, Ch16.
- [25] L. Guo, G. S. Guvanasen, X. Liu, C. Tuthill, T. R. Nichols, S. P. DeWeerth, in *IEEE Transactions on Biomedical Circuits and Systems*, Vol. 7, IEEE, USA 2013, NO. 1.
- [26] I. Nam, S. Bae, S. Park, Y. G. Yoo, J. M. Lee, J. W. Han, J. Yi, *Nano Energy* 2015, 15, 33.
- [27] B. Zhu, H. Wang, W. R. Leow, Y. Cai, X. J. Loh, M. Y. Han, X. Chen, *Adv. Mater.* 2015, 28, 1559.
- [28] Z. Niu, W. Zhou, X. Chen, J. Chen, S. Xie, *Adv. Mater.* 2015, 27, 6002.
- [29] D. McCoul, W. Hu, M. Gao, V. Mehta, Q. Pei, *Adv. Electron. Mater.* 2016, doi: 10.1002/aelm.201500407.
- [30] X. Wang, Z. Xiong, Z. Liu, T. Zhang, *Adv. Mater.* 2015, 27, 1467.
- [31] F. Xu, W. Lu, Y. Zhu, *ACS Nano* 2010, 5, 672.
- [32] M. Zarek, M. Layani, I. Cooperstein, E. Sachyani, D. Cohn, S. Magdassi, *Adv. Mater.* 2015, 28, 4449.
- [33] R. C. Webb, A. P. Bonifas, A. Behnaz, Y. Zhang, K. J. Yu, H. Cheng, M. Shi, Z. Bian, Z. Liu, Y.-S. Kim, *Nature Mater.* 2013, 12, 938.
- [34] H. Y. Jang, S.-K. Lee, S. H. Cho, J.-H. Ahn, S. Park, *Chem. Mater.* 2013, 25, 3535.
- [35] C. Chen, W. Tao, Y. Su, J. Wu, J. Song, *J. Appl. Mech.* 2013, 80, 041031.
- [36] J. Mertens, R. W. Bowman, J. C. Willis, A. Robinson, D. Cotton, R. White, K. A. Seffen, J. J. Baumberg, *Phys. Rev. Appl.* 2015, 4, 044006.
- [37] C. F. Guo, T. Sun, Q. Liu, Z. Suo, Z. Ren, *Nature Commun.* 2014, 5, 3132.
- [38] P. Lee, J. Ham, J. Lee, S. Hong, S. Han, Y. D. Suh, S. E. Lee, J. Yeo, S. S. Lee, D. Lee, *Adv. Funct. Mater.* 2014, 24, 5671.
- [39] J. Kim, M. Lee, H. J. Shim, R. Ghaffari, H. R. Cho, D. Son, Y. H. Jung, M. Soh, C. Choi, S. Jung, *Nature Commun.* 2014, 5, 5747.

- [40] J. Vanfleteren, F. Bossuyt, T. Löher, Y.-Y. Hsu, M. Gonzalez, J. Günther, in *Stretchable Electronics* (Ed: T. Someya), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany 2012, Ch9.
- [41] J. A. Fan, W.-H. Yeo, Y. Su, Y. Hattori, W. Lee, S.-Y. Jung, Y. Zhang, Z. Liu, H. Cheng, L. Falgout, M. Bajema, T. Coleman, D. Gregoire, R. J. Larsen, Y. Huang, J. A. Rogers, *Nature Commun.* 2014, 5, 3266.
- [42] S. Wagner, S. Bauer, *MRS Bull.* 2012, 37, 207.
- [43] D. J. Lipomi, *Adv. Mater.* 2015, 28, 4180.
- [44] A. Romeo, Q. Liu, Z. Suo, S. P. Lacour, *Appl. Phys. Lett.* 2013, 102, 131904.
- [45] S. Savagatrup, A. D. Printz, T. F. O'Connor, A. V. Zaretski, D. J. Lipomi, *Chem. Mater.* 2014, 26, 3028.
- [46] J. W. Boley, E. L. White, G. T. C. Chiu, R. K. Kramer, *Adv. Funct. Mater.* 2014, 24, 3501.
- [47] Y. Zhang, S. Xu, H. Fu, J. Lee, J. Su, K.-C. Hwang, J. A. Rogers, Y. Huang, *Soft Matter* 2013, 9, 8062.
- [48] J. Vanfleteren, M. Gonzalez, F. Bossuyt, T. Vervust, I. De Wolf, M. Jablonski In *PCB technology based stretchable circuits*, EIPC Summer Conference, 2013.
- [49] M. Melzer, D. Karnaushenko, G. Lin, S. Baunack, D. Makarov, O. G. Schmidt, *Adv. Mater.* 2015, 27, 1333.
- [50] S. H. Jeong, A. Hagman, K. Hjort, M. Jobs, J. Sundqvist, Z. Wu, *Lab Chip* 2012, 12, 4657.
- [51] C. Keplinger, J.-Y. Sun, C. C. Foo, P. Rothemund, G. M. Whitesides, Z. Suo, *Science* 2013, 341, 984.
- [52] H. B. Lee, C. W. Bae, L. T. Duy, I. Y. Sohn, D. I. Kim, Y. J. Song, Y. J. Kim, N. E. Lee, *Adv. Mater.* 2016, 28, 3069.
- [53] H.-J. Kim, C. Son, B. Ziaie, *Appl. Phys. Lett.* 2008, 92, 011904.
- [54] N. Matsuhisa, M. Kaltenbrunner, T. Yokota, H. Jinno, K. Kuribara, T. Sekitani, T. Someya, *Nature Commun.* 2015, 6, 7461.
- [55] A. J. Bandonkar, R. Nuñez-Flores, W. Jia, J. Wang, *Adv. Mater.* 2015, 27, 3060.
- [56] D. Y. Khang, J. A. Rogers, H. H. Lee, *Adv. Funct. Mater.* 2009, 19, 1526.
- [57] T. Someya, *Stretchable electronics*. John Wiley & Sons: 2012.
- [58] T. Li, Z. Huang, Z. Suo, S. P. Lacour, S. Wagner, *Appl. Phys. Lett.* 2004, 85, 3435.

- [59] O. Akogwu, D. Kwabi, A. Munhutu, T. Tong, W. Soboyejo, J. Appl. Phys. 2010, 108, 123509.
- [60] O. Van Der Sluis, Y.-Y. Hsu, P. Timmermans, M. Gonzalez, J. Hoefnagels, J. Phys. D: Appl. Phys. 2010, 44, 034008.
- [61] B. G. Vossen, P. J. Schreurs, O. van der Sluis, M. Geers, J. Mech. Phys. Solids 2014, 66, 117.
- [62] X. Lu, Y. Xia, Nature Nanotech. 2006, 1, 163.
- [63] J. Song, H. Jiang, Z. J. Liu, D. Y. Khang, Y. Huang, J. A. Rogers, C. Lu, C. G. Koh, Inter. J. Solids Struct. 2008, 45, 3107.
- [64] C. C. Fu, A. Grimes, M. Long, C. G. Ferri, B. D. Rich, S. Ghosh, S. Ghosh, L. P. Lee, A. Gopinathan, M. Khine, Adv. Mater. 2009, 21, 4472.
- [65] P. Görrn, W. Cao, S. Wagner, Soft Matter 2011, 7, 7177.
- [66] S. P. Lacour, J. Jones, S. Wagner, T. Li, Z. Suo, Proc. IEEE 2005, 93, 1459.
- [67] J. Brandrup, E. H. Immergut, E. A. Grulke, A. Abe, D. R. Bloch, Polymer handbook. Wiley New York: 1999, Vol. 89.
- [68] Z. Liu, M. Yu, J. Lv, Y. Li, Z. Yu, ACS Appl. Mater. Interfaces 2014, 6, 13487.
- [69] Z. Liu, D. Qi, P. Guo, Y. Liu, B. Zhu, H. Yang, Y. Liu, B. Li, C. Zhang, J. Yu, B. Liedberg, X. Chen, Adv. Mater. 2015, 27, 6230.

Chapter 9

Discussion and Future Work

In this chapter, the preliminary results of stretchable conductor encapsulation and related effects on the stretchability and sensitivity are discussed. Also, the interfacial brittle layer is introduced to further enhance the sensitivity and linearity of the stretchable strain sensor. At last, the future work in order to obtain the long-term stable soft stretchable electrodes and sensors is discussed.

9.1 General Discussion

In this thesis, it mainly addresses how to achieve the stretchable electrodes and strain sensors based on the new proposed strategy: surface strain regulation to release the strain energy by numerous micro fractures keeping the conductive network at the same time. Different new methods are developed based on this new strategy which already prove the efficiency of this strategy.

Firstly, the hypothesis of controlling the surface strain distribution is proposed and analyzed, and the feature of this strategy is stated. The importance of achieving stretchable electrodes and strain sensors is elucidated. Also, the methods which are employed to do the study are discussed including the polymer preparation, surface modification, thermal evaporation, electrical testing technologies, and so on.

Based on this strategy, five new methods are developed: three of them for achieving stretchable active materials, and two for sensor performance enhancement. In detail, carbon nanotubes network by coffee ring effect, nanopiles interlocking, and dynamic interface mingling are the new methods proposed to achieve stretchable conductors. Hair-like sensors and fiber-shaped sensors are the new methods for new kinds of sensors and enhancing the performance.

The carbon nanotube was employed as the active material and a very straightforward method, coffee ring effect, to fabricate stretchable carbon nanotube film with gradient thickness was developed. The detailed performance data is presented and so are the principles. It is based on constructing the film with gradient thickness, which couples the seemingly contrary properties of brittleness and stretchability together to fabricate strain sensors with high gauge factor and large stretchability. The thickness-gradient film was formed by employing self-pinning effect of the single wall carbon nanotube solution. The fabricated sensor possesses surprisingly good performance covering all requirements of the sensitivity, stretchability and long-term stability. In this method, the surface strain regulation in the active materials is achieved by self-assembled carbon nanotube network structure itself. The randomly distributed defects form during the coffee ring process, after that, they grow into micro fractures when tensile strain applied.

Stretchable hair-like sensors based on the three-dimensional coffee ring effect are proposed. In this work, the surface strain regulation is utilized to detect the strain applied direction. The fine hair on human body or animal skins is quite an excellent strain sensor. It can detect very tiny strain, e.g., the one induced by gentle wind. It would be important if this sensing function can be mimicked. The sensor fabrication and performance data is presented and discussed here. the 3D stretchable tactile electronic hairs (e-hairs) with isotropic stretchability, which can detect multiple strains and the strain direction (any direction) with high sensitivity and stability by each single e-hair, and the unique underlying detection principle relies on the symmetry breaking of the resistance network at the root. Besides, the fabrication process is all-solution based by employing 3D printing and a capillary force-assisted self-pinning of carbon nanotubes. The e-hairs can be easily fabricated in an array format for efficient monitoring of gas and liquid flow. Furthermore, fiber-shaped stretchable strain sensors based on coffee ring effect of carbon nanotubes and micro-cracked stretchable gold film are developed. In this work, by surface strain regulation, the strain concentration is induced at certain locations which enhances the sensitivity significantly. This work tends to shift the vision of improving the sensitivity of the stretchable strain sensor from the active materials engineering to the mechanical design of the elastic substrate. A novel strategy that enables surface strain redistribution in elastic substrate to significantly enhance the sensitivity is introduced. Such enhancement method attributes to the delicate structure of beads on a fiber based on the principle of Plateau-Rayleigh instability. Also, a new method of transient thermal curing is proposed for large-scale fabrication of PDMS fibers with predefined diameter.

Another new method to achieve the surface strain regulation achieving the stretchability, named nanopiles interlocking is proposed. In this work, the nanopiles interlocking layer serves as the transitional layer to tune the strain distribution mode in the active material to achieve the stretchability and high adhesion simultaneously. Inspired by a tree, a new method is proposed to fabricate high-adhesion stretchable electrodes that can be used as strain sensors with tunable stretchability, high gauge factor and stability. The nanopile not only provides the interlocking effect to significantly improve the adhesion, but also ensures that the tensile strain in the film is redistributed to release the strain energy by random cracks forming the connecting network and achieving the stretchability.

Lastly, the new method based on the strategy of surface strain regulation, dynamic interface mingling, is developed to activate the synchronous forming of metal film and polymer at the interface. Dynamic interface mingling of elastic polymer and metal is utilized to fabricate stretchable conductors with high stretchability and stability, high surface area and most importantly, high adhesion between the metal, gold, and elastic polymer, Polydimethylsiloxane (PDMS). The underlying knack is to use uncured PDMS instead of fully cured one to receive the gold atoms generated by the thermal evaporation. It will trigger a series of dynamic chemical and physical processes fabricating stretchable conductors with the unique microstructure of self-stripped kalst caves-like double layers and the superior performance. The micro pillars in the cave will regulate the strain distribution in the active material to achieve the surface strain regulation achieving the stretchability.

As discussed in the Chapter 2, it would be a long way to go to achieve the reliable real-time monitoring of bio-electrical and mechanical signals. To fabricate soft stretchable electrodes and strain sensors are the very beginning step. Next would be how to fabricate the long-term stable electrodes and sensors.

9.2 Brittle layer to significantly enhance the sensitivity of stretchable strain sensors not included in main chapters

9.2.1 Brittle layer induced on PDMS

The main objective was to improve the sensitivity and the linear region of the sensor. Firstly, a copper foil mask with a 0.6cm*0.6 cm hole in the middle was adhered to the PDMS film (3cm*1.1cm). Then the sample underwent surface plasma treatment with 5 mbar oxygen pressure and 1000w for 12min to make the PDMS film hydrophilic and, more importantly, form a brittle layer on the PDMS substrate. Then the mask was peeled off. The following step was to drop 2 μ l SWCNT solution onto the hydrophilic surface. After 20 min, a coffee ring pattern would be formed. Another sample was fabricated. All procedures were the same as the first sample in method 3, except that this sample didn't use the 0.6cm*0.6 cm mask.

A control sample was also fabricated as a reference. Firstly, a copper foil mask with a

0.6cm*0.6 cm hole in the middle was adhered to the PDMS film (3cm*1.1cm). Then the sample underwent surface plasma treatment with 5 mbar oxygen pressure and 500w for 30s to make the PDMS film hydrophilic. Then the mask was peeled off. The following step was to drop 2 μ l SWCNT solution onto the hydrophilic surface. After 20 min, a coffee ring pattern would be formed. And the process is displayed in Figure 9.1.

Figure 9.1 Plasma Induced Brittle Layer Process.

Finally, all three samples' resistance was measured versus strain with the use of MTS strain machine and Keithley electronic device.

9.2.2 Sensitivity significantly enhanced

Figure 9.2 a: The Illustration of Coffee Ring; b: The Illustration of a Sample Clipped in the MTS Strain Machine; c: The Illustration of a Sample with Brittle Layer at Small Strain; d: The Illustration of a Sample with Brittle Layer at Large Strain

In this method, the plasma induced brittle surface layer was used to improve the sensitivity of the sensor. Figure 9.2a shows a coffee ring clearly, where its CNT thickness increased from inside to the outer rim. And figure 22b shows a sample being clipped inside the MTS strain machine, and the resistance would be recorded down while the sample was being stretched. Figure 9.2c and 9.2d displays the morphology of the sample at small strain and large strain respectively. And there was an obvious difference between them. That is at larger strain, various colors like rainbow appeared. This was due to the young's modulus of the brittle surface layer was different from that of PDMS base, so the wavelength was different, and thus the rainbow would appear due to interference of wavelength. And the brittle layer was able to tune the cracking behavior and thus increase the sensitivity and linear region.

Figure 9.3 a: The SEM Image of the CNT Part of a Sample with Brittle Layer; b: The SEM Image of the CNT part of a sample without Brittle Layer

Figure 9.3a and 9.3b show the SEM image of the CNT part of sample with and without brittle layer respectively. It is clearly shown that the wavelength of the sample without brittle layer was much shorter than the one with brittle layer. So the stretchability of the sample without brittle layer is higher than the one with brittle layer, and thus the sensitivity is higher. The principle can be explained as the relationship between the wavelength and fracture toughness. The longer the wavelength, the flatter the film would be, the less the wrinkled structure, so strain energy could only be dissipated via propagating the crack instead of consuming the strain energy of the wrinkled structure. Therefore, the stretchability was lower, and thus the sensitivity was higher.

Figure 9.4 a: The SEM Image of the CNT Part of a Sample with Brittle Layer with Mask; b: The SEM Image of the PDMS Part of a Sample with Brittle Layer with Mask; c: The SEM Image of the CNT Part of a Sample with Brittle Layer without Mask; d: The SEM Image of the PDMS Part of a Sample with Brittle Layer without Mask

Figure 9.3c and 9.3d shows the SEM image of the CNT part and PDMS part of a sample both with brittle layer but without mask respectively. The vertical lines represent the wavelength and wrinkled structure. And the horizontal lines represent the cracks. It could be observed that their cracking behaviors were quite similar to each other, and same phenomenon occurred in figure a and b, where shows the SEM image of the CNT part and PDMS part of a sample with brittle layer and mask respectively. In normal case, where the sample didn't generate a brittle surface layer, the main mechanism to control the sensitivity was due to the CNT gradient film, or in other words, the wrinkled structure. However, in the case where brittle layer generated, the brittle layer played the main role to control the sensitivity of the sensor by tuning the cracking behavior. Whereas CNT gradient film played the second important role.

In return, the availability to form SEM image of the PDMS part proved the generation of brittle layer. It was impossible to take the SEM image of the normal PDMS base without brittle layer, since it was not crystalline. So it was electric insulating. Therefore, it proved

that brittle layer was able to exhibit certain crystalline and electrical conductive properties that made it possible to form SEM images.

And Figure 9.4a and 9.4b shows the SEM image of the CNT part and PDMS part of a sample with brittle layer but without mask respectively. The cracking behaviors were also quite similar to each other, just like the sample with mask. So this proved that the O_2 plasma at 1000w for 12min was too strong for the mask to protect the covered PDMS film from interaction with the O_2 . By observing the micromorphology, even the sample with mask still formed a brittle layer on the total area of the film.

9.3 Encapsulation for stretchable electronics

9.3.1 Encapsulation employed

Three samples with different parameters were fabricated. First one didn't have any encapsulation layer on the CNT film, second one was covered with an undiluted PDMS encapsulation layer, and third one was covered with a diluted PDMS (weight ratio of hexane to PDMS: 7:3) encapsulation layer (Figure 9.5). Sample with undiluted encapsulation layer was put into oven at 60°C for 24 hours, and sample with diluted encapsulation layer was put into oven at 60°C for 48 hours.

Figure 9.5 Encapsulation process of the stretchable strain sensor.

Finally, all three samples' resistance was measured versus strain with the use of MTS strain machine and Keithley electronic device

9.3.2 Preliminary results for the stretchable strain sensor

Figure 9.6 a: The Relationship between resistance ratio and strain within 10% strain; b: The relationship between resistance ratio and strain within 30% Strain; c: The relationship between resistance ratio and strain within 60% strain.

According to the assumption, encapsulation was supposed to increase the gauge factor via restricting the generation of wrinkle and thus making the film less stretchable. And another function of the encapsulation was expected to increase the stability of the sample.

However, the first function failed to reach target, and what's worse, the gauge factor decreased, both with undiluted and diluted encapsulation, according to figure 20. The reason for failure of undiluted encapsulation method might be due to the large thickness of PDMS layer. The large thickness of the PDMS layer caused the change of strain distribution on the film. In other words, the strain of the internal CNT film covered by encapsulation was actually smaller than it was supposed to be. As a result, the sensitivity would decrease. And the reason for the decrease of sensitivity of diluted PDMS layer was

due to the interaction of PDMS with the hexane solvent, which might strongly influence the sensitivity of the sensor. What's worse, the thickness was still too high, so it could influence the strain distribution just like that of the undiluted encapsulation. However, as can be seen from the graph, the larger the strain, the closer the gauge factor value between undiluted and diluted PDMS layer, as can be seen in Figure 9.6. This may indicate that the interaction between hexane and PDMS would become weaker when further stretching the sensor.

However, the other objective, which was to increase the stability of the sensor has been successfully achieved according to Figure 9.7. Figure 9.7 shows the comparison between the sample with undiluted encapsulation one month before and after. As can be seen clearly from the figure, at 0% strain, the resistance of sample after one month ($15\text{k}\Omega$) was only around 1.5 times higher than that of the original one ($10\text{k}\Omega$). As for the sample without encapsulation, however, the resistance of sample after one month ($9.6\text{k}\Omega$) was more than 10 times higher than that of the original one ($0.88\text{k}\Omega$), which was measured via Ohmmeter. This was because that the PDMS encapsulation layer was hydrophobic, which could insulate CNT film from moisture and thus prevent it from degrading its electronic performance.

Figure 9.7 a: Initial resistance-strain performance with undiluted encapsulation; b: Resistance-strain performance after one month with undiluted encapsulation.

9.4 Future work: long-term implantation of the electrode and long-term stable stretchable strain sensors

In the near future, when the central and peripheral neural systems are reliably connected with the external, i.e., the two-way communication is achieved, both more precise diagnoses and abundant therapies would be realized. For diagnose, it is common to receive the signal detection of electroencephalogram, electromyography and electrocardiogram in the clinic, however due to the decay effect of the skin and bone, the *in-vitro* signal loses some precise information compared to that detected *in vivo*. Besides, for some applications, e.g., brain stimulation, the *in-vivo* testing by implanting the electrode to exactly investigate which neuro is firing for the study of functions of some neural circuits is required (for animal model at present). For therapy, since the relationship between the neural electro-stimulation and the immune system is recently revealed, electroceuticals was proposed hopefully to treat some diseases only by neural stimulation, and tiny implanted flexible electrodes were reported to be designed for this function. Meanwhile, some famous pharmacy companies, like Glaxosmithkline, start to explore the related product. It could be quite close to the traditional Chinese therapy: acupuncture. It has been used in China for thousands of years but the working mechanism is still not clear until now. They all make use of external stimulation to initiate the human body to recover. How to take advantage of the stretchable electrode in the acupuncture could be another important task. Furthermore, the neural regeneration in spinal cord, alleviating the Parkinsonian symptoms, deep brain stimulation and recording, the configuration of the artificial retina could be achieved by implanting stretchable electrodes.

It is still a long way to go to fully make use of the stretchable electrode and other devices based on it, and it will change the interaction with the electric devices. It could endow the electronic device with personifications that is with tactile, smell, and other sensations.