Heterogeneous strain distribution of elastomer substrates to enhance the sensitivity of stretchable strain sensors

Jiang, Ying; Liu, Zhiyuan; Wang, Changxian; Chen, Xiaodong

2019

Jiang, Y., Liu, Z., Wang, C., & Chen, X. (2019). Heterogeneous strain distribution of elastomer substrates to enhance the sensitivity of stretchable strain sensors. *Accounts of Chemical Research*, 52(1), 82-90. doi:10.1021/acs.accounts.8b00499

<https://hdl.handle.net/10356/137809>

<https://doi.org/10.1021/acs.accounts.8b00499>

This document is the Accepted Manuscript version of a Published Work that appeared in final form in *Accounts of Chemical Research*, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <https://doi.org/10.1021/acs.accounts.8b00499>

Downloaded on 26 Apr 2023 14:17:02 SGT

Heterogeneous Strain Distribution of Elastomer Substrates to Enhance Sensitivity of Stretchable Strain Sensors

*Ying Jiang, Zhiyuan Liu, Changxian Wang, Xiaodong Chen**

Innovative Centre for Flexible Devices (iFLEX), School of Materials Science and Engineering,
Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

Conspectus: Stretchable strain sensors which convert mechanical stimuli into electrical signal, largely fuel the growth of wearable bioelectronics, due to the ubiquitous, health-related strain in biological system. In contrast to rigid conventional strain sensors, stretchable strain sensors present advantages

of conformality and stretchability, solving the mechanical mismatch between electronics and human body. Yet the great challenge of stretchable strain sensors lies in achieving high sensitivity, which is required for both signal fidelity and cost consideration. Recent advances to solve this sensitivity challenge focus on material optimization, in search of optimum combination with both conductive active materials and elastomer substrates, among a myriad of artificial or natural

materials. However, high sensitivity with gauge factor larger than 50 remains a grand challenge, especially within large strain region.

Here we present heterogeneous strain distribution of elastomer substrates as a powerful strategy to significantly enhance sensitivity in stretchable strain sensors. The theoretical foundation of this strategy is mathematically proven based on Ohm's law in electrics and mechanics of materials. Firstly, extent of sensitivity enhancement is proved to be determined by local strain in resistance-testing segments of heterogeneous strain sensors. Next, local strain is proved to be quantitatively decided by material properties such as section area and Young's modulus. Thus, the necessary and sufficient condition to achieve high sensitivity in heterogeneous strain sensors is that Young's modulus reciprocal or section area reciprocal in resistance-testing segment is larger than the mean value. This provides a theoretical design guideline to achieve high sensitivity via heterogeneous strain distribution.

Based on this guideline, we systematically summarize concrete instances of heterogeneity-induced sensitivity improvement in stretchable strain sensors, in sequence of dimensions. A typical example of one-dimensional heterogeneous strain sensors is the structured fiber with microbeads, where varied section area along fiber axis results in heterogeneous strain and sensitivity improvement. Two-dimensional heterogeneous sensors in form of thin film contain thickness gradient sensors and auxetic mechanical metamaterial sensors. The former exhibits heterogeneous section area via self-pinning method, while the auxetic sensors show heterogeneity in both strain direction and amplitude, leading to a 24-fold improvement in sensitivity. Three-dimensional strain sensors include rationally structured sensor for out-of-plane force detection, and asymmetric active materials in electronic whisker. The resultant enhanced sensitivity in these heterogeneous strain sensors is beneficial for such applications as continuous health monitoring,

biomedical diagnostics, replacement prosthetics, taking advantages of augmented detection accuracy and declined device cost. Finally, we discuss possible future work in exploiting heterogeneous strain distribution, involving extended methodology to achieve heterogeneity, employing suppressed strain for stretchable electrodes, cyclic durability for long-term application, and multifunctional system-level integration. We believe this strategy of heterogeneous strain distribution to enhance sensitivity can strongly promote the development of stretchable strain sensors, for both practical and theoretical requirements.

1. Introduction

Stretchable strain sensors transduce mechanical strain stimuli into readable electrical signals, thus attracted tremendous attention in recent years. Since their softness and stretchability solve the mechanical mismatch between electronics and biological organs, stretchable strain sensors exhibit enormous potential in wearable, healthcare bioelectronics (**Figure 1a**).¹⁻⁴ For example, motion-related neurological disorders can be diagnosed via stretchable strain sensors, which controls drug-delivery system as a feedback therapy.⁵ However, the greatest challenge of stretchable strain sensors towards practical applications lies in sensitivity limitation (**Figure 1b**).⁶ Here sensitivity or gauge factor (GF) in resistive-type sensor is defined as $GF = (\Delta R/R_0)/\varepsilon$, where $\Delta R/R_0$ represents relative resistance change under applied strain ε . Capacitive-type sensors are not discussed in this review, since their exhibit very low sensitivity due to theoretical limitations. The sensitivity limitation restrains sensor accuracy in wearable bioelectronics, because minor yet valuable strain details would be lost during signal transduction. Besides, low sensitivity largely increases demand for post-processing circuit, raising the cost exponentially. Therefore, there is a strong need for developing strategy to enhance sensitivity in stretchable strain sensors to fulfill practical requirements.

Recently, researchers have developed various methods to enhance sensitivity of stretchable strain sensors, mostly based on material optimization. These material optimization methods can be classified into two strategies, based on different components in stretchable strain sensors. The first strategy refers to optimization of active material, which renders strain sensing capability via electrical resistance change. The choice of active materials ranges from low dimensional materials (carbon nanotubes (CNT),^{2,3,7} silver nanoparticles (AgNP),^{8,9} graphene,^{10,11} carbon black,^{12,13} and Fullerene¹⁴), metal thin films or networks (gold nanowires,^{15,16} silver nanowires¹⁷), to liquid

metal¹⁸ and ionic liquid composite.¹⁹ For instance, carbonized silk fabric with excellent conductivity was employed in stretchable strain sensors, with gauge factor of 9.6 within 250% strain and 37.5 for 250-500% strain.²⁰ The second strategy is optimization of substrate material, which serves as stretchable platform and provide stretchability in stretchable strain sensors. The requirement for substrate material is that their mechanical properties should be similar to applied surface as human skin, in order to transduce strain with high sensitivity. Therefore, flexible or stretchable polymers are often chosen and modified, such as polyethylene terephthalate (PET),²¹ Ecoflex,^{22,23} polydimethylsiloxane (PDMS)^{24,25} and so on. For instance, highly conformal and extensible elastomeric matrices were developed in 3D-printed stretchable strain sensor, achieving gauge factor of 3.8 ± 0.6 for 100% applied strain.²⁶ In addition, diminishing sensor thickness to tens of micrometers also improves sensitivity, because conformal contact with curvilinear human skin minimizes strain signal loss during transmission.^{27,28}

Figure 1. (a). Ubiquitous strain in human body as biological input for stretchable strain sensors, including vocal cord vibration, heart contraction, and joint motion. (b). Challenge in stretchable strain sensors lies in sensitivity limitation, requiring high relative resistance change upon applied

strain. Vocal cord phonation diagram: Reproduced with permission from ref. 29. Copyright 2018 Dreamstime Inc.. Heart contraction diagram: Reproduced with permission from ref 30. Copyright 2015 John Wiley and Sons. Joint motion diagram: Reproduced with permission from ref. 31. Copyright 2013 John and Wiley and Sons.

Though these material optimization strategies achieved incremental progress in sensitivity enhancement, the achievable gauge factor is still limited, and high sensitivity of $GF > 50$ remains a grand challenge in stretchable strain sensors. Here we summarize the recent development in using heterogeneous strain distribution in elastomer substrate to enhance sensitivity in stretchable strain sensors. Firstly, the theoretical foundation of this strategy was mathematically derived based on electrics and mechanics. Then, a general design guideline was put forward, showing how to obtain such heterogeneous sensor via different material properties. Next, following this design guideline, we reviewed recent advances in heterogeneous strain sensors with high sensitivity, in sequence of dimensions. Lastly, challenges and future directions are discussed for practical implementation. We believed that this heterogeneity-induced highly sensitive stretchable strain sensors would shed light on wearable bioelectronics, as well as fundamental medical sciences in the near future.

2. Theoretical Foundation for Sensitivity Enhancement in Heterogeneous Strain Sensors

To address the challenge of sensitivity limitation, heterogeneous strain sensors were developed as an improvement of conventional homogeneous sensors. Here we present the theoretical foundation to prove that heterogeneous strain distribution of elastomer substrate can enhance sensitivity, compared with homogeneous sensor. More interestingly, we raise a quantitative guideline to design such heterogeneous sensor, via modulating properties such as Young's modulus and section area. In this mathematical derivation, one-dimensional stretchable strain sensor was used for simplicity, while higher dimensional cases can be qualitatively deducted

following the same logic, with parameters changing from vector to tensor. Both homogeneous and heterogeneous sensors are divided into N segments, with length Δl and resistance R_{i0} of one segment i . In conventional homogeneous sensors, gauge factor GF_{hetero} depends on resistance measured on two ends, while gauge factor GF_{hetero} in heterogeneous sensors only counts on resistance of segment i .

Firstly, the relationship between sensitivity and local strain is investigated (**Figure 2a**). From definition, when strain ε_0 is exerted on two ends, gauge factor of homogeneous and heterogeneous sensors can be expressed as:

$$GF_{homo} = \frac{1}{\varepsilon_0} * (R_{homo} - N * R_{i0}) / (N * R_{i0}) \quad (1)$$

$$GF_{hetero} = \frac{1}{\varepsilon_0} * (R_{hetero} - R_{i0}) / R_{i0} \quad (2)$$

Where R_{homo} and R_{hetero} are resistance upon strain in homogeneous and heterogeneous sensor, respectively. Taken resistance in one segment as a function of local strain ε_i , we can rewrite the resistance expression: $R_{homo} = N * R(\varepsilon_0)$, $R_{hetero} = R(\varepsilon_i)$, because in homogeneous sensor local strain equals to total strain ε_0 . In all stretchable strain sensors as far as we know, $R(\varepsilon)$ is a monotonic increasing function. Thus the necessary and sufficient condition for $GF_{hetero} > GF_{homo}$ is that local strain in segment i is larger than total strain:

$$GF_{hetero} > GF_{homo} \Leftrightarrow \varepsilon_i > \varepsilon_0 \quad (3)$$

Next, we quantitatively examine the relationship between local strain ε_i and material properties, in order to acquire a guideline to design heterogeneous sensor (**Figure 2b**). From fundamental mechanics, total strain ε_0 can be expressed as function of local strain ε_j via formula

$\varepsilon_0 = \left(\frac{1}{L}\right) * \sum_{j=1}^N (\varepsilon_j * \Delta l)$, where L and Δl are total length and segment length, respectively.

Meanwhile, from definition of Young's modulus, local strain ε_i in segment i can be expressed as:

$\varepsilon_i = \frac{P_i}{E_i * A_i}$, where P_i , E_i and A_i are pressure, Young's modulus and section area in segment i ,

respectively. In equilibrium state, pressure P_i should be the same for every segment, expressed as

$P_i \equiv P_0$ where P_0 is a constant. Therefore, local strain ε_i can be expressed as function of E_i and A_i :

$$\varepsilon_i = \varepsilon_i(E_i, A_i) = \frac{\varepsilon_0 * L}{E_i A_i \sum_{j=1}^N \frac{\Delta l}{E_j A_j}} \quad (4)$$

From pure mathematical derivation from equation (2) and (3), the necessary and sufficient condition for $GF_{hetero} > GF_{homo}$ is that:

$$GF_{hetero} > GF_{homo} \Leftrightarrow \varepsilon_i > \varepsilon_0 \Leftrightarrow \begin{cases} \frac{1}{A_i} > \overline{\left(\frac{1}{A}\right)} & \text{when } E_i \equiv E_0 \\ \frac{1}{E_i} > \overline{\left(\frac{1}{E}\right)} & \text{when } A_i \equiv A_0 \end{cases} \quad (5)$$

Where $\overline{\left(\frac{1}{A}\right)} = \left(\frac{1}{L}\right) * \sum_{j=1}^N (\Delta l / A_j)$ is the mean value of section area reciprocal $1/A$, and $\overline{\left(\frac{1}{E}\right)} = \left(\frac{1}{L}\right) *$

$\sum_{j=1}^N (\Delta l / E_j)$ is the mean value of Young's modulus reciprocal $1/E$. The physical meaning of this

condition is quite intuitive: in heterogeneous sensor, when and only when Young's modulus reciprocal or section area reciprocal in segment i is larger than average, gauge factor would be

larger than in homogeneous sensors. In addition, strain concentration phenomenon may lead to

deviation in exact value of local strain, which needs to be considered in specific cases. This

derivation provides a sensor design guideline to quantitatively design highly-sensitive

heterogeneous stretchable strain sensors with various detection ranges, via material properties

modulation.

Figure 2. Theoretical derivation to prove sensitivity enhancement due to heterogeneous design.

(a). Under total strain ϵ_0 , gauge factor in homogeneous sensor GF_{homo} depends on resistance measured on two ends, while GF_{hetero} in heterogeneous sensor depends on resistance in one segment. Both gauge factors are positively correlated to strain in resistance measurement region.

(b). Local strain ϵ_i can be mathematically expressed as function of material properties (Young's modulus E_i and section area A_i). This provides a guideline to design heterogeneous stretchable strain sensors, in pursuit of sensitivity enhancement. Homogeneous design and heterogeneous design. Reproduced with permission from ref. 32. Copyright 2017 John Wiley and Sons.

3. One-dimensional (1D) Heterogeneous Sensor

Based on the aforementioned theoretical derivation, a heterogeneous 1D strain sensor was developed, which modulates section area to obtain heterogeneous strain distribution and consequent sensitivity enhancement (**Figure 3a**).³² While measuring electrical resistance at segments in-between microbeads, the condition of $\frac{1}{A_i} > \overline{\left(\frac{1}{A}\right)} = \left(\frac{1}{L}\right) * \sum_{j=1}^N (\Delta l/A_j)$ is satisfied, leading to strain concentration and sensitivity enhancement, compared with homogeneous bare fiber.

Figure 3. Structured microfibers as heterogeneous one-dimensional stretchable strain sensor. (a). Heterogeneous strain distribution from FEA shows local strain concentration at the microfiber segments in-between microbeads, which is further verified by gold microcrack in SEM images. (b). Heterogeneous fiber manifests significantly longer crack length compared with homogeneous sensors. (c). Heterogeneity can be increased by modulating bead diameter, providing flexibility for gauge factor enhancement. Reproduced with permission from ref. 32. Copyright 2017 John Wiley and Sons.

Experimentally, such heterogeneous fiber-based stretchable strain sensor was fabricated via transient thermal curing method. The as-prepared smooth PDMS fiber was dipped into viscous PDMS precursor, and microbeads were automatically formed due to Plateau-Rayleigh instability. By subsequent transient thermal curing, it forms microstructured PDMS fiber with heterogeneous section area. To achieve strain sensing capability, gold film was thermally deposited on one side

of the fiber as active material. The theoretical strain concentration in heterogeneous fiber-shaped sensor was proved by both finite element analysis (FEA) and microcrack investigation (**Figure 3b**). Microcracks became much longer and wider on heterogeneous microstructured fiber, compared to homogeneous smooth fiber. The heterogeneous fiber sensor exhibits good gauge factor as high as 25, compared with gauge factor of merely 10 in homogeneous smooth sensor (**Figure 3c**). This sensitivity improvement is in consistence with theoretical prediction, where higher section area reciprocal $\frac{1}{A}$ in microfiber in-between microbeads leads to higher local strain, thus enhancing sensitivity. The heterogeneous design can be applied to other active materials. Gauge factor of 100 can be achieved with CNT as active material under 10% strain, an enhancement from 50 in homogeneous sensors. In addition, by increasing microbeads diameter or decreasing microfiber diameter, the heterogeneity can be further improved, providing a feasible approach for flexible sensitivity enhancement.

Such 1D heterogeneous stretchable strain sensors with high sensitivity is promising for health monitoring smart textile, due to their good compatibility with existing textile technologies such as weaving, knitting, embroidery and sewing.^{20,33-35} For example, smart glove integrated with stretchable strain sensors can recognize human gestures via finger motion detection, promising for human-machine interactions.⁴ The sensitivity enhancement in virtue of heterogeneous strain distribution, would lead to higher detection accuracy as well as lower cost of these smart textiles.

4. Two dimensional (2D) Heterogeneous Sensor

2D stretchable strain sensors in the form of thin film are extensively exploited, due to their compatibility with existing thin film technology, and mechanical compliance to nonplanar human

tissues. In this case, the theoretical foundation for heterogeneous strain distribution still holds qualitatively, with all variables as functions of plane coordinates. Therefore, we can rationally design the heterogeneous strain distribution via material structural properties, in order to solve the sensitivity challenge.

As a typical example, thickness gradient stretchable strain sensors was reported with heterogeneous section area, exhibiting both high sensitivity and stretchability (**Figure 4a**).³⁶ This thickness gradient was generated via self-pinning method, also called coffee ring effect. During evaporation of CNT suspension on PDMS substrate, capillary flow drives CNT from middle to the sides, forming thickness gradient in CNT ring (**Figure 4b**). The thin thickness of ~25 nm in inner region makes it transparent in optical photo, while outer rim is black with the largest thickness of ~250 nm (**Figure 4c, d**). This thickness gradient results in heterogeneous section area, thus demonstrates largely enhanced gauge factor as high as 161 under 2% strain (Figure 4e). In sharp contrast, homogeneous sensor with thick region cut off shows gauge factor of only 2.8. This significant sensitivity enhancement enables recognition for small strain vibration such as in weak sound detection, expanding the application scope for bioelectronics.

Figure 4. Heterogeneous stretchable strain sensor with thickness gradient. (a). Self-pinning effect forms thickness gradient in CNT active material, resulted from the capillary flow during evaporation. (b). Thickness gradient is characterized by surface profile curve. (c, d). Optical and SEM images show transparent inner region with low thickness, and black outer rim with large thickness. (e). Thickness gradient stretchable strain sensor exhibits high gauge factor with good cyclic durability. Reproduced with permission from ref. 36. Copyright 2015 John Wiley and Sons.

Auxetic mechanical metamaterials can also be employed for heterogeneous stretchable strain sensors for high sensitivity, due to the synergistic effect of both heterogeneity in strain direction and amplitude (**Figure 5a**).³⁷ Experimentally, auxetic mechanical metamaterial sensors were composed of PDMS auxetic frame, PDMS thin film and CNT layer in the middle area as conductive active material. Firstly, the heterogeneous strain direction comes from reduced

structural Poisson's ratio (**Figure 5b**). In conventional sensor, the flat and homogeneous film encounter transverse Poisson compression under strain. Alternatively, auxetic metamaterials tend to expand in both longitudinal and transverse direction. This 2D expansion tendency leads to reduced structural Poisson's ratio and heterogeneous strain direction. Secondly, heterogeneous strain amplitude comes from the regulatory effect of auxetic metamaterial frame, showing strain concentration in CNT area. In contrast, conventional homogeneous sensor exhibits nearly uniform strain distribution (**Figure 5c**). Together, heterogeneity in both strain direction and amplitude synergistically enhanced sensitivity of auxetic metamaterial sensors. Gauge factor of auxetic sensors reached as high as 835 under 15% strain, a 24-fold improvement over homogeneous sensor with gauge factor of merely 35 (**Figure 5d**).

Figure 5. Auxetic mechanical metamaterials for heterogeneous stretchable strain sensors. (a, b). Auxetic mechanical metamaterials shows expansion in two directions, while conventional flat thin film endures transverse Poisson compression upon strain. (c). Auxetic metamaterial sensor exhibits obvious strain concentration under FEA, in contrast to uniform strain in homogeneous one. (d). Synergistic effect of heterogeneity in both strain direction and amplitude results in significant sensitivity enhancement. In auxetic metamaterial sensor, high gauge factor of 835 is achieved under 15% strain, a 24-fold improvement over homogeneous flat sensor. Reproduced with permission from ref. 37. Copyright 2018 John Wiley and Sons.

This high sensitivity in virtue of heterogeneous strain distribution allows broad applications for medical diagnostics, replacement prosthetic device or biomedical soft robotics.^{38,39} For instance, human radial wave detection was achieved with high fidelity and abundant medical details, by auxetic metamaterial sensors (**Figure 6a**). The signal-to-noise ratio (SNR) in auxetic sensor is much larger than homogeneous sensor due to its high sensitivity (**Figure 6b**). Hence valuable medical information was preserved via auxetic metamaterial sensor, which is beneficial for accurate and continuous health monitoring (**Figure 6c, d**). Other examples of 2D strain sensors with heterogeneous strain distribution also exhibit similar sensitivity enhancement and advantageous performance in health monitoring.^{40,41}

Figure 6. High sensitivity from heterogeneous strain distribution enables high fidelity for bioelectronics. (a). Auxetic metamaterial strain sensor for radial pulse detection. Scale bar: 5 mm (left), 1cm (right). (b). Enhanced signal-to-noise (SNR) ratio in auxetic metamaterial sensor, compared with homogeneous flat sensor. (c, d). Abundant medical details were detected via auxetic metamaterial strain sensor, including forward wave, peak systolic pressure, and discretic notch, in virtue of heterogeneity-induced high sensitivity. Reproduced with permission from ref. 37. Copyright 2018 John Wiley and Sons.

5. Three-dimensional (3D) Heterogeneous Sensor

While 2D stretchable strain sensors perceive mechanical strain within the sensor plane, out-of-plane force detection can only be achieved via 3D strain sensors.^{1,8,42-46} Such out-of-plane force detection is found to be ubiquitous in nature, such as air/liquid flow detection in spiders or Venus

flytrap. In this case, heterogeneous strain distribution should be considered and obtained from a three-dimensional perspective. From previous theoretical design guideline, material properties such as Young's modulus and section area can be rationally modulated to form heterogeneous three-dimensional distribution.

A representative example is the 3D-structured stretchable strain sensors with capability of tensile, compression, bending detection, as well as strain direction recognition (**Figure 7a**).⁴² As initial basic structure, design I was composed of elastomer pillar inserted into substrate. After inducing heterogeneity in Young's modulus and section area, the optimized design IV exhibits obvious strain concentration in root area (**Figure 7b**). As anticipated, in heterogeneous design, sensitivity was largely enhanced to 10 at 45° bending angle, compared with merely 4 in homogeneous design (**Figure 7c**). Taking advantages of this high sensitivity, wind or water flow speed can be reliably recognized, with strain details such as flow turbulence and shutting off disturbance (**Figure 7d**). Such heterogeneous 3D-structured strain sensor shows great promise in air/liquid flow rate measurement in stretchable microfluidics, since high sensitivity is strongly required for subtle flow within micro- or nano-liter scales.

Figure 7. 3D-structured heterogeneous strain sensor for out-of-plane force detection. (a). Design optimization within structure I-IV, inducing heterogeneity in both section area and Young's modulus. (b). FEA shows effective strain concentration in root area with active materials. (c). Sensitivity in terms of relative resistance change upon bending is largely enhanced via structural optimization. (d). The high sensitivity enables water flow detection with recognition of laminar and turbulent flow, beneficial for stretchable microfluidics. Reproduced with permission from ref. 42. Copyright 2018 John Wiley and Sons.

Another example for 3D heterogeneous strain sensor presented highly sensitive electronic whiskers (e-whisker) via asymmetric active materials (**Figure 8a**).⁸ The e-whisker consists of PDMS fiber, and CNT-AgNP composite was coated on both top and bottom surfaces as active

material. Upon bending, the two surfaces experience opposite strain (tensile and compressive), forming intrinsic heterogeneous strain distribution. Therefore, the resistance changes from top and bottom surfaces were canceled out with each other, resulting in failure to detect bending strain (**Figure 8b**). Here heterogeneous active material was induced to match up with the heterogeneous strain in substrate, with high-sensitive active materials coated on top, and low-sensitive materials on bottom (**Figure 8c**). This heterogeneity enables e-whiskers to detect bending strain from gas flow with high sensitivity, showing relative resistance change of 40% under tip pressure of 2.5 Pa^{1/2} (**Figure 8d**). In this way, heterogeneity from both mechanical properties and electrical properties together enhance the sensitivity of e-whiskers, compared to total sensing incapability in sensors with homogeneous active materials.

Figure 8. Heterogeneous highly sensitive electronic whisker with asymmetric active materials.

(a). Symmetric active materials in electronic whiskers, with same resistance in top and bottom

electrodes. (b). Upon bending, top and bottom electrodes endure opposite strains (compressive and tensile), leading to disability for strain detection. (c). Heterogeneous active materials are deposited to match up with heterogeneous strain, with resistance on top electrode more sensitive than bottom electrode. (d). Upon bending, only resistance change of top electrodes affects sensor output, thus enables capability for strain detection with high sensitivity. Reproduced with permission from ref. 8. Copyright 2013 United States National Academy of Sciences.

6. Conclusion and Perspectives

In this Account, we systematically summarized heterogeneous strain distribution as an effective approach to solve the sensitivity challenge of stretchable strain sensors. Theoretical foundation proved that, sensitivity can be enhanced through heterogeneous strain distribution, which can be quantitatively regulated via material properties. Concrete examples of heterogeneous stretchable strain sensors were presented, in the order of dimension. The various implementation methods consist of structured microfibers, thickness gradient, auxetic mechanical metamaterials, out-of-plane 3D structure, and asymmetric materials. Despite of these progress, several challenges and potential future directions towards practical implementations are listed as blow.

(1). More extensive approaches could be developed to realize heterogeneous strain distribution and subsequent enhanced sensitivity. One possible approach is to employ heterogeneous mechano-responsive materials into stretchable strain sensors, for example, ionic conductive hydrogels with heterogeneous swelling ratio. Another promising approach is to obtain heterogeneous strain in terms of time domain, for instance, by employing various components with different response time. Recent advances in 3D or 4D printing with increasingly diverse printing materials and resolution may be contributive in such heterogeneous design.

(2). Other than stretchable strain sensors, heterogeneous strain distribution can also be employed in stretchable electrodes, which requires low resistance change upon applied strain. In this way, the suppressed local strain from heterogeneous electrodes could preserve integrity of electron pathway under strain.^{47,48} These stretchable electrodes exhibit great potential as conductive interconnects, battery current collectors or transistor electrodes, favorable for wearable bioelectronics.

(3). Other challenges confronted stretchable strain sensors include cyclic durability and skin irritation. Cyclic durability is easy to be deteriorated due to delamination between active materials and low energy elastomer surface, thus reliable adhesive interface was required.^{49,50} Skin irritation may occur when skin-mountable devices prevent sweating and block airflow from skin pores, where biocompatible nanocomposites with oxidation-resistivity⁵¹ or air permeability⁵² should be employed.

(4). Integration towards stretchable system constitutes an area of tremendous opportunity, in the future of highly sensitive stretchable strain sensors. Multiple functionalities should be rendered into healthcare system by incorporating various stretchable sensors.⁵³ Also, development for stretchable circuit components will be necessary, including stretchable data storage, wireless data transmission, and power supply.⁵⁴ Furthermore, data analysis should combine the high-fidelity data together with advanced algorithms such as deep learning, in order to increase accuracy and specificity for personalized diagnostics.

In summary, the heterogeneous strain distribution of elastomer substrate can significantly enhance sensitivity in stretchable strain sensors. These highly sensitive stretchable strain sensors will accelerate advancements in practical applications such as health monitoring, preventive

diagnostics and subsequent therapeutics, as well as boosting in-depth understanding in fundamental physiology and pathology.

Corresponding author

***chenxd@ntu.edu.sg**

ORCID

Xiaodong Chen: 0000-0002-3312-1664

Biographical Information

Ying Jiang is currently a Ph.D. student at School of Materials Science and Engineering, Nanyang Technological University, Singapore, under supervision of Prof. X. Chen. She received her B.S. degree in microelectronics from Sun Yat-sen University (China) in 2012, and M.S. degree in physics from Tsinghua University (China) in 2015. Her research interests focus on mechanical metamaterials and stretchable healthcare devices.

Zhiyuan Liu is currently a postdoctoral fellow in the School of Materials Science and Engineering at Nanyang Technological University, Singapore. He received his B.Eng. degree in thermal engineering in 2009 and M.Eng. degree in engineering thermophysics in 2012 from the Harbin Institute of Technology (China), and PhD degree from Nanyang Technological University, Singapore in 2017. His current research focuses on flexible devices for sensing and bio-electrophysiology.

Changxian Wang is currently a postdoctoral fellow in School of Materials Science and Engineering at Nanyang Technological University, Singapore. He received his B.S. degree in flight vehicle design and engineering from Harbin Engineering University (China) in 2013, and Ph.D. degree in

solid mechanics from the Peking University (China) in 2018. His research interests focus on stretchable multi-functional devices.

Xiaodong Chen is a Professor at Nanyang Technological University, Singapore. He received his B.S. degree in chemistry from Fuzhou University (China) in 1999, M.S. degree in physical chemistry from the Chinese Academy of Sciences in 2002, and Ph.D. degree in biochemistry from the University of Muenster (Germany) in 2006. After working as a postdoctoral fellow at Northwestern University (USA), he started his independent research career as a Singapore National Research Foundation Fellow and Nanyang Assistant Professor at Nanyang Technological University in 2009. He was promoted to Associate Professor in 2013 and Full Professor in 2016. His research interests include Integrated nano-bio interface and programmable materials for energy conversion.

ACKNOWLEDGMENTS: The authors thank the financial support from the National Research Foundation, Prime Minister's Office, Singapore under its NRF Investigatorship (NRF2016NRF-NRFI001-21) and Singapore Ministry of Education (MOE2015-T2-2-060).

REFERENCES

- (1) Pang, C.; Lee, G.-Y.; Kim, T.-i.; Kim, S. M.; Kim, H. N.; Ahn, S.-H.; Suh, K.-Y. A flexible and highly sensitive strain-gauge sensor using reversible interlocking of nanofibres. *Nature Mater.* **2012**, *11*, 795-801.
- (2) Lipomi, D. J.; Vosgueritchian, M.; Tee, B. C. K.; Hellstrom, S. L.; Lee, J. A.; Fox, C. H.; Bao, Z. Skin-like pressure and strain sensors based on transparent elastic films of carbon nanotubes. *Nature Nanotech.* **2011**, *6*, 788-792.
- (3) Yamada, T.; Hayamizu, Y.; Yamamoto, Y.; Yomogida, Y.; Izadi-Najafabadi, A.; Futaba, D. N.; Hata, K. A stretchable carbon nanotube strain sensor for human-motion detection. *Nature Nanotech.* **2011**, *6*, 296-301.
- (4) Chen, S.; Lou, Z.; Chen, D.; Jiang, K.; Shen, G. Polymer-Enhanced Highly Stretchable Conductive Fiber Strain Sensor Used for Electronic Data Gloves. *Adv. Mater. Technol.* **2016**, *1*, 1600136.
- (5) Son, D.; Lee, J.; Qiao, S.; Ghaffari, R.; Kim, J.; Lee, J. E.; Song, C.; Kim, S. J.; Lee, D. J.; Jun, S. W.; Yang, S.; Park, M.; Shin, J.; Do, K.; Lee, M.; Kang, K.; Hwang, C. S.; Lu, N.

Hyeon, T.; Kim, D.-H. Multifunctional wearable devices for diagnosis and therapy of movement disorders. *Nature Nanotech.* **2014**, *9*, 397-404.

(6) Amjadi, M.; Kyung, K.-U.; Park, I.; Sitti, M. Stretchable, Skin-Mountable, and Wearable Strain Sensors and Their Potential Applications: A Review. *Adv. Funct. Mater.* **2016**, *26*, 1678-1698.

(7) Li, Q.; Liu, C.; Lin, Y.-H.; Liu, L.; Jiang, K.; Fan, S. Large-Strain, Multiform Movements from Designable Electrothermal Actuators Based on Large Highly Anisotropic Carbon Nanotube Sheets. *ACS Nano* **2015**, *9*, 409-418.

(8) Takei, K.; Yu, Z.; Zheng, M.; Ota, H.; Takahashi, T.; Javey, A. Highly sensitive electronic whiskers based on patterned carbon nanotube and silver nanoparticle composite films. *Proc. Natl. Acad. Sci. U.S.A.* **2014**, *111*, 1703-1707.

(9) Yang, Z.; Wang, D.-Y.; Pang, Y.; Li, Y.-X.; Wang, Q.; Zhang, T.-Y.; Wang, J.-B.; Liu, X.; Yang, Y.-Y.; Jian, J.-M.; Jian, M.-Q.; Zhang, Y.-Y.; Yang, Y.; Ren, T.-L. Simultaneously Detecting Subtle and Intensive Human Motions Based on a Silver Nanoparticles Bridged Graphene Strain Sensor. *ACS Appl. Mater. Interfaces* **2018**, *10*, 3948-3954.

(10) Wang, Y.; Wang, L.; Yang, T.; Li, X.; Zang, X.; Zhu, M.; Wang, K.; Wu, D.; Zhu, H. Wearable and Highly Sensitive Graphene Strain Sensors for Human Motion Monitoring. *Adv. Funct. Mater.* **2014**, *24*, 4666-4670.

(11) Zhao, J.; Wang, G.; Yang, R.; Lu, X.; Cheng, M.; He, C.; Xie, G.; Meng, J.; Shi, D.; Zhang, G. Tunable Piezoresistivity of Nanographene Films for Strain Sensing. *ACS Nano* **2015**, *9*, 1622-1629.

(12) Lu, N.; Lu, C.; Yang, S.; Rogers, J. Highly Sensitive Skin-Mountable Strain Gauges Based Entirely on Elastomers. *Adv. Funct. Mater.* **2012**, *22*, 4044-4050.

(13) Kong, J.-H.; Jang, N.-S.; Kim, S.-H.; Kim, J.-M. Simple and rapid micropatterning of conductive carbon composites and its application to elastic strain sensors. *Carbon* **2014**, *77*, 199-207.

(14) Shi, X.; Liu, S.; Sun, Y.; Liang, J.; Chen, Y. Lowering Internal Friction of 0D-1D-2D Ternary Nanocomposite-Based Strain Sensor by Fullerene to Boost the Sensing Performance. *Adv. Funct. Mater.* **2018**, *28*, 1800850.

(15) Gong, S.; Lai, D. T. H.; Su, B.; Si, K. J.; Ma, Z.; Yap, L. W.; Guo, P.; Cheng, W. Highly Stretchy Black Gold E-Skin Nanopatches as Highly Sensitive Wearable Biomedical Sensors. *Adv. Electron. Mater.* **2015**, *1*, 1400063.

(16) Ho, M. D.; Ling, Y.; Yap, L. W.; Wang, Y.; Dong, D.; Zhao, Y.; Cheng, W. Percolating Network of Ultrathin Gold Nanowires and Silver Nanowires toward “Invisible” Wearable Sensors for Detecting Emotional Expression and Apexcardiogram. *Adv. Funct. Mater.* **2017**, *27*, 1700845.

(17) Amjadi, M.; Pichitpajongkit, A.; Lee, S.; Ryu, S.; Park, I. Highly Stretchable and Sensitive Strain Sensor Based on Silver Nanowire-Elastomer Nanocomposite. *ACS Nano* **2014**, *8*, 5154-5163.

(18) Cooper, C. B.; Arutselvan, K.; Liu, Y.; Armstrong, D.; Lin, Y.; Khan, M. R.; Genzer, J.; Dickey, M. D. Stretchable Capacitive Sensors of Torsion, Strain, and Touch Using Double Helix Liquid Metal Fibers. *Adv. Funct. Mater.* **2017**, *27*, 1605630.

(19) Choi, D. Y.; Kim, M. H.; Oh, Y. S.; Jung, S.-H.; Jung, J. H.; Sung, H. J.; Lee, H. W.; Lee, H. M. Highly Stretchable, Hysteresis-Free Ionic Liquid-Based Strain Sensor for Precise Human Motion Monitoring. *ACS Appl. Mater. Interfaces* **2017**, *9*, 1770-1780.

(20) Wang, C.; Li, X.; Gao, E.; Jian, M.; Xia, K.; Wang, Q.; Xu, Z.; Ren, T.; Zhang, Y.

Carbonized Silk Fabric for Ultrastretchable, Highly Sensitive, and Wearable Strain Sensors. *Adv. Mater.* **2016**, *28*, 6640-6648.

(21) Sun, Q.; Seung, W.; Kim, B. J.; Seo, S.; Kim, S.-W.; Cho, J. H. Active Matrix Electronic Skin Strain Sensor Based on Piezopotential-Powered Graphene Transistors. *Adv. Mater.* **2015**, *27*, 3411-3417.

(22) Morteza, A.; Yong Jin, Y.; Inkyu, P. Ultra-stretchable and skin-mountable strain sensors using carbon nanotubes–Ecoflex nanocomposites. *Nanotechnology* **2015**, *26*, 375501.

(23) Ryu, S.; Lee, P.; Chou, J. B.; Xu, R.; Zhao, R.; Hart, A. J.; Kim, S.-G. Extremely Elastic Wearable Carbon Nanotube Fiber Strain Sensor for Monitoring of Human Motion. *ACS Nano* **2015**, *9*, 5929-5936.

(24) Li, X.; Yang, T.; Yang, Y.; Zhu, J.; Li, L.; Alam, F. E.; Li, X.; Wang, K.; Cheng, H.; Lin, C.-T.; Fang, Y.; Zhu, H. Large-Area Ultrathin Graphene Films by Single-Step Marangoni Self-Assembly for Highly Sensitive Strain Sensing Application. *Adv. Funct. Mater.* **2016**, *26*, 1322-1329.

(25) Kim, K. K.; Hong, S.; Cho, H. M.; Lee, J.; Suh, Y. D.; Ham, J.; Ko, S. H. Highly Sensitive and Stretchable Multidimensional Strain Sensor with Prestrained Anisotropic Metal Nanowire Percolation Networks. *Nano Lett.* **2015**, *15*, 5240-5247.

(26) Muth, J. T.; Vogt, D. M.; Truby, R. L.; Mengüç, Y.; Kolesky, D. B.; Wood, R. J.; Lewis, J. A. Embedded 3D Printing of Strain Sensors within Highly Stretchable Elastomers. *Adv. Mater.* **2014**, *26*, 6307-6312.

(27) Kim, D.-H.; Lu, N.; Ma, R.; Kim, Y.-S.; Kim, R.-H.; Wang, S.; Wu, J.; Won, S. M.; Tao, H.; Islam, A.; Yu, K. J.; Kim, T.-i.; Chowdhury, R.; Ying, M.; Xu, L.; Li, M.; Chung, H.-J.; Keum, H.; McCormick, M.; Liu, P.; Zhang, Y.-W.; Omenetto, F. G.; Huang, Y.; Coleman, T.; Rogers, J. A. Epidermal Electronics. *Science* **2011**, *333*, 838-843.

(28) Hanif, A.; Trung, T. Q.; Siddiqui, S.; Toi, P. T.; Lee, N.-E. Stretchable, Transparent, Tough, Ultrathin, and Self-limiting Skin-like Substrate for Stretchable Electronics. *ACS Appl. Mater. Interfaces* **2018**, *10*, 27297-27307.

(29) Website of Dreamstime, Vocal cords, www.dreamstime.com (accessed: September 2018).

(30) Nguyen, M. M.; Carlini, A. S.; Chien, M.-P.; Sonnenberg, S.; Luo, C.; Braden, R. L.; Osborn, K. G.; Li, Y.; Gianneschi, N. C.; Christman, K. L. Enzyme-Responsive Nanoparticles for Targeted Accumulation and Prolonged Retention in Heart Tissue after Myocardial Infarction. *Adv. Mater.* **2015**, *27*, 5547-5552.

(31) Claes, S.; Vereecke, E.; Maes, M.; Victor, J.; Verdonk, P.; Bellemans, J. Anatomy of the anterolateral ligament of the knee. *J. Anat.* **2013**, *223*, 321-328.

(32) Liu, Z.; Qi, D.; Hu, G.; Wang, H.; Jiang, Y.; Chen, G.; Luo, Y.; Loh, X. J.; Liedberg, B.; Chen, X. Surface Strain Redistribution on Structured Microfibers to Enhance Sensitivity of Fiber-Shaped Stretchable Strain Sensors. *Adv. Mater.* **2017**, *30*, 1704229.

(33) Liao, X.; Liao, Q.; Zhang, Z.; Yan, X.; Liang, Q.; Wang, Q.; Li, M.; Zhang, Y. A Highly Stretchable ZnO@Fiber-Based Multifunctional Nanosensor for Strain/Temperature/UV Detection. *Adv. Funct. Mater.* **2016**, *26*, 3074-3081.

(34) Zhong, J.; Zhong, Q.; Hu, Q.; Wu, N.; Li, W.; Wang, B.; Hu, B.; Zhou, J. Stretchable Self-Powered Fiber-Based Strain Sensor. *Adv. Funct. Mater.* **2015**, *25*, 1798-1803.

(35) Matsuhisa, N.; Kaltenbrunner, M.; Yokota, T.; Jinno, H.; Kuribara, K.; Sekitani, T.; Someya, T. Printable elastic conductors with a high conductivity for electronic textile applications. *Nat. Commun.* **2015**, *6*, 7461.

- (36) Liu, Z.; Qi, D.; Guo, P.; Liu, Y.; Zhu, B.; Yang, H.; Liu, Y.; Li, B.; Zhang, C.; Yu, J.; Liedberg, B.; Chen, X. Thickness-Gradient Films for High Gauge Factor Stretchable Strain Sensors. *Adv. Mater.* **2015**, *27*, 6230-6237.
- (37) Jiang, Y.; Liu, Z.; Matsuhisa, N.; Qi, D.; Leow, W. R.; Yang, H.; Yu, J.; Chen, G.; Liu, Y.; Wan, C.; Liu, Z.; Chen, X. Auxetic Mechanical Metamaterials to Enhance Sensitivity of Stretchable Strain Sensors. *Adv. Mater.* **2018**, *30*, 1706589.
- (38) Trung, T. Q.; Lee, N.-E. Flexible and Stretchable Physical Sensor Integrated Platforms for Wearable Human-Activity Monitoring and Personal Healthcare. *Adv. Mater.* **2016**, *28*, 4338-4372.
- (39) Roh, E.; Hwang, B.-U.; Kim, D.; Kim, B.-Y.; Lee, N.-E. Stretchable, Transparent, Ultrasensitive, and Patchable Strain Sensor for Human-Machine Interfaces Comprising a Nanohybrid of Carbon Nanotubes and Conductive Elastomers. *ACS Nano* **2015**, *9*, 6252-6261.
- (40) Fu, Y.-F.; Li, Y.-Q.; Liu, Y.-F.; Huang, P.; Hu, N.; Fu, S.-Y. High-Performance Structural Flexible Strain Sensors Based on Graphene-Coated Glass Fabric/Silicone Composite. *ACS Appl. Mater. Interfaces* **2018**, *10*, 35503-35509.
- (41) Liao, X.; Zhang, Z.; Kang, Z.; Gao, F.; Liao, Q.; Zhang, Y. Ultrasensitive and stretchable resistive strain sensors designed for wearable electronics. *Materials Horizons* **2017**, *4*, 502-510.
- (42) Liu, Z.; Qi, D.; Leow, W. R.; Yu, J.; Xiloyannis, M.; Cappello, L.; Liu, Y.; Zhu, B.; Jiang, Y.; Chen, G.; Masia, L.; Liedberg, B.; Chen, X. 3D-Structured Stretchable Strain Sensors for Out-of-Plane Force Detection. *Adv. Mater.* **2018**, *30*, 1707285.
- (43) Hua, Q.; Liu, H.; Zhao, J.; Peng, D.; Yang, X.; Gu, L.; Pan, C. Bioinspired Electronic Whisker Arrays by Pencil-Drawn Paper for Adaptive Tactile Sensing. *Adv. Electron. Mater.* **2016**, *2*, 1600093.
- (44) Zhang, J.; Hao, L.; Yang, F.; Jiao, W.; Liu, W.; Li, Y.; Wang, R.; He, X. Biomimic Hairy Skin Tactile Sensor Based on Ferromagnetic Microwires. *ACS Appl. Mater. Interfaces* **2016**, *8*, 33848-33855.
- (45) Peleshanko, S.; Julian, M. D.; Ornatska, M.; McConney, M. E.; LeMieux, M. C.; Chen, N.; Tucker, C.; Yang, Y.; Liu, C.; Humphrey, J. A. C.; Tsukruk, V. V. Hydrogel-Encapsulated Microfabricated Haircells Mimicking Fish Cupula Neuromast. *Adv. Mater.* **2007**, *19*, 2903-2909.
- (46) Harada, S.; Honda, W.; Arie, T.; Akita, S.; Takei, K. Fully Printed, Highly Sensitive Multifunctional Artificial Electronic Whisker Arrays Integrated with Strain and Temperature Sensors. *ACS Nano* **2014**, *8*, 3921-3927.
- (47) Romeo, A.; Liu, Q.; Suo, Z.; Lacour, S. P. Elastomeric substrates with embedded stiff platforms for stretchable electronics. *Appl. Phys. Lett.* **2013**, *102*, 131904.
- (48) Vandeparre, H.; Liu, Q.; Mineev, I. R.; Suo, Z.; Lacour, S. P. Localization of Folds and Cracks in Thin Metal Films Coated on Flexible Elastomer Foams. *Adv. Mater.* **2013**, *25*, 3117-3121.
- (49) Liu, Z.; Wang, X.; Qi, D.; Xu, C.; Yu, J.; Liu, Y.; Jiang, Y.; Liedberg, B.; Chen, X. High-Adhesion Stretchable Electrodes Based on Nanopile Interlocking. *Adv. Mater.* **2016**, *29*, 1603382.
- (50) Li, J.; Celiz, A. D.; Yang, J.; Yang, Q.; Wamala, I.; Whyte, W.; Seo, B. R.; Vasilyev, N. V.; Vlassak, J. J.; Suo, Z.; Mooney, D. J. Tough adhesives for diverse wet surfaces. *Science* **2017**, *357*, 378-381.
- (51) Choi, S.; Han, S. I.; Jung, D.; Hwang, H. J.; Lim, C.; Bae, S.; Park, O. K.; Tschabrunn, C. M.; Lee, M.; Bae, S. Y.; Yu, J. W.; Ryu, J. H.; Lee, S.-W.; Park, K.; Kang, P. M.;

Lee, W. B.; Nezafat, R.; Hyeon, T.; Kim, D.-H. Highly conductive, stretchable and biocompatible Ag–Au core–sheath nanowire composite for wearable and implantable bioelectronics. *Nature Nanotech.* **2018**, *13*, 1048-1056.

(52) Miyamoto, A.; Lee, S.; Cooray, N. F.; Lee, S.; Mori, M.; Matsuhisa, N.; Jin, H.; Yoda, L.; Yokota, T.; Itoh, A.; Sekino, M.; Kawasaki, H.; Ebihara, T.; Amagai, M.; Someya, T. Inflammation-free, gas-permeable, lightweight, stretchable on-skin electronics with nanomeshes. *Nature Nanotech.* **2017**, *12*, 907-913.

(53) Boutry, C. M.; Kaizawa, Y.; Schroeder, B. C.; Chortos, A.; Legrand, A.; Wang, Z.; Chang, J.; Fox, P.; Bao, Z. A stretchable and biodegradable strain and pressure sensor for orthopaedic application. *Nat. Electron.* **2018**, *1*, 314-321.

(54) Yun, J.; Song, C.; Lee, H.; Park, H.; Jeong, Y. R.; Kim, J. W.; Jin, S. W.; Oh, S. Y.; Sun, L.; Zi, G.; Ha, J. S. Stretchable array of high-performance micro-supercapacitors charged with solar cells for wireless powering of an integrated strain sensor. *Nano Energy* **2018**, *49*, 644-654.