



From Design to Applications of Stimuli-Responsive Hydrogel Strain Sensors

| | |
|-------------------------------|--|
| Journal: | <i>Journal of Materials Chemistry B</i> |
| Manuscript ID | TB-REV-11-2019-002692.R1 |
| Article Type: | Review Article |
| Date Submitted by the Author: | 03-Jan-2020 |
| Complete List of Authors: | Zhang, Dong; University of Akron, Chemical, Biomolecular, and Corrosion Engineering Ren, Baiping; University of Akron Zhang, Yanxian; University of Akron Xu, Lijian; Hunan University of Technology Huang, Qinyuan; Sichuan University of Science and Engineering He, Yi; Zhejiang University, College of Chemical and Biological Engineering Li, Xuefeng; Hubei University of Technology, Wu, Jiang; Wenzhou Medical University, School of Pharmaceutical Sciences Yang, Jintao; Zhejiang University of Technology Chen, Qiang; Henan Polytechnic University, Materials Science and Engineering Chang, Yung; Chung Yuan Christian University, Chemical Engineering Zheng, Jie; University of Akron, Chemical, Biomolecular, and Corrosion Engineering |
| | |

From Design to Applications of Stimuli-Responsive Hydrogel Strain Sensors

Dong Zhang¹ζ, Baiping Ren¹ζ, Yanxian Zhang¹, Lijian Xu², Qinyuan Huang³, Yi He⁴, Xuefeng Li⁵, Jiang Wu⁶, Jintao Yang⁷, Qiang Chen⁸, Yung Chang⁹, and Jie Zheng^{1*}

¹ Department of Chemical, Biomolecular, and Corrosion Engineering
The University of Akron, Ohio 44325, USA

² Hunan Key Laboratory of Biomedical Nanomaterials and Devices
College of Life Science and Chemistry
Hunan University of Technology, Zhuzhou 412007, China

³ School of Automation and Information Engineering
Sichuan University of Science and Engineering, Zigong, Sichuan 643000, P. R. China

⁴ College of Chemical and Biological Engineering
Zhejiang University, Zheda Road 38, Hangzhou 310027, China

⁵ School of Material Science and Chemical Engineering
Hubei University of Technology, Wuhan 430068, P. R. China

⁶ School of Pharmaceutical Sciences
Wenzhou Medical University, Wenzhou, Zhejiang 325035, China

⁷ College of Materials Science & Engineering
Zhejiang University of Technology, Hangzhou 310014, China

⁸ School of Material Science and Engineering
Henan Polytechnic University, Jiaozuo, 454003 China

⁹ Department of Chemical Engineering and R&D Center for Membrane Technology
Chung Yuan Christian University, Taoyuan 320, Taiwan

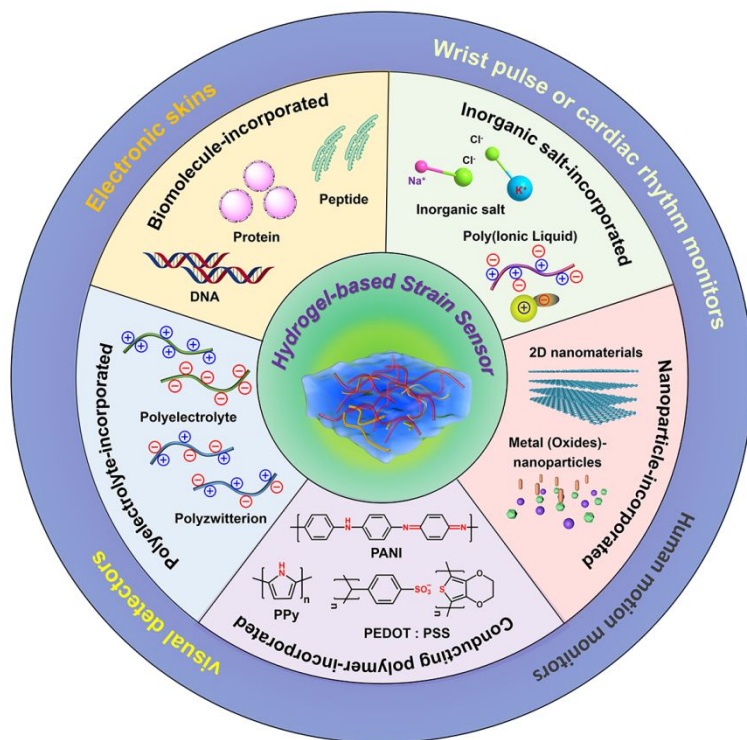
ζ These authors contribute equally to this work.

* Corresponding Authors: zhengj@uakron.edu

Abstract

Stimuli-responsive hydrogel strain sensors that synergizes the advantages of both soft-wet hydrogels and smart functional materials have attracted rapidly growing interests for exploring the opportunities from materials design principles to emerging applications in electronic skins, health monitors, and human-machine interfaces. Stimuli-responsive hydrogel strain sensors possess smart and on-demand ability to specifically recognize various external stimuli and convert them into strain-induced mechanical, thermal, optical, and electrical signals. This review presents an up-to-date summery over the past five years on hydrogel strain sensors from different aspects, including materials designs, gelation/fabrication methods, stimuli-responsive principles, and sensing performance. Hydrogel strain sensors are classified into five major categories based on the nature of stimuli, and representative examples from each category are carefully selected and discussed in terms of structures, response mechanisms, and potential medical applications. In the end, current challenges and future perspectives of hydrogel strain sensors are tentatively proposed to stimulate the more and better research in this emerging field.

Table of Contents



1. Introduction

Hydrogels, as classical soft-wet materials containing a high-water content in flexible, 3D networks, possess many structural and functional advantages of hierarchical porous structures, viscoelasticity, transparency, stretchability, and biocompatibility. Particularly, recent studies have pushed the potential applications and development of hydrogels from traditional fields of cell/tissue scaffolds¹⁻⁴, drug/gene delivery carriers⁵⁻⁷, wound dressings⁸⁻¹¹, and contact lenses¹²⁻¹⁴ to emerging fields of wearable devices¹⁵⁻¹⁷, electronic skins¹⁸⁻¹⁹, soft robotics²⁰⁻²², and artificial intelligence sensors²³. Among them, stimuli-responsive hydrogel strain sensors have attracted significant and continuous efforts to be developed as a promising platform for disease diagnosis, health monitoring, damage/motion detection, water/food safety, and environmental monitoring²⁴⁻²⁸, because of their intelligent and programmable features capable of changing their shape/size/volume and probably other functional properties (e.g. conductivity, permeability, viscosity, and mechanics) in response to different stimuli. Different from those dry sensors made of elastomers, polymer/inorganic composites, and carbon-based materials without water, the presence of a high-water content enables hydrogel strain sensors to exhibit intrinsic swelling-induced viscoelastic, mechanical, self-recovery, self-healing properties²⁹⁻³⁶, rendering them great potentials to realize a variety of sensing actuations under different stimuli³⁷. On the other hand, due to high hydration nature of hydrogel sensors, all of stimuli-responsive polymers, crosslinkers, and incorporated entities need to be compatible with and workable under the wet or aqueous conditions. Another major difference is that mismatching mechanics among polymer networks, additives, and crosslinkers with different swollen extents at polymer/water interfaces will create asymmetric forces that drive shape and volume changes of the hydrogels even under subtle stimuli.

From a materials design viewpoint, all stimuli-responsive hydrogels could be potentially fabricated into hydrogel-based sensors. Several general design strategies have been proposed and demonstrated for the successful development of a wide variety of hydrogel sensors. First, a most commonly used design is to directly fabricate stimuli-responsive materials into hydrogels, which are sensitive to external stimuli of temperature, pH, salt, light, and electric. Several typical stimuli-responsive hydrogels include thermo-responsive poly(*N*-isopropylacrylamide) (polyNIPAM) and poly(vinyl methyl ether) (polyVME) hydrogels, pH-responsive carboxylated poly(2-hydroxyethyl methacrylate-ethylene glycol dimethacrylate) (poly(HEMA-EDMA)) hydrogels³⁸, electronic-responsive conducting polymers-based (CPs) hydrogels³⁹, light/force-sensitive poly(acrylamide (AAM)-*co*-methyl acrylate (MA))/spiropyran (SP) hydrogels⁴⁰⁻⁴¹, and salt-responsive poly([2-(methacryloyloxy) ethyl]- trimethylammonium chloride)-[*N*-(2-hydroxyethyl) acrylamide])/ poly(3-(1-(4-vinylbenzyl)-1H-benzo[d]imidazol-3-ium-3-yl)-propane-1-sulfonate) (poly(METAC-HEAA)/polyVBIPS) and polyNIPAM/ polyVBIPS hydrogels⁴²⁻⁴³. Advances in chemical synthesis and gelation methods also allow to copolymerize or sequentially polymerize different stimuli-responsive monomers and crosslinkers to achieve dual or multiple stimuli-responsive properties embedded in hydrogel sensors, including polyAAM/poly(vinylalcohol)(PVA) humidity sensor⁴⁴, poly(β -cyclodextrin (β -CD)-methacrylic acid (AAc)) hydrogels⁴⁵, and Eu³⁺/Tb³⁺-polyNIPAM hydrogel⁴⁶. In general, since hydrogels are typically isotropic materials, use of pure polymer materials or simple polymer structures are unlikely to selectively trigger site-specific swelling or contraction, leading to shape adaptability and transformation in a controllable manner. To overcome this issue, another common design strategy is to incorporate stimuli-

responsive entities (i.e. nanoparticles, nanoclay, nano-crystalline cellulose, and functional polymer chains) into hydrogel networks to create in-homogeneous structures, which in turn help to readily generate mismatch stress for a strain sensing purpose under the desired stimuli. These stimuli-responsive entities can be either physically added into or chemically crosslinked with hydrogel networks, both of which require the controlled orientation and spatial distribution to achieve well-defined network architectures and to maximize the sensibility to external stimuli. But, additional difficulty of snug-filling of small entities into hydrogel porous structures was needed to overcome for preventing dead zones upon deformation.

From a structural design viewpoint, constructing hybrid network structures in the hydrogel sensors, such as double-network structure, bilayer/multi-layer structure, interpenetrating structure, nanofilled structure, gradient structure, and other heterostructures, also allows to create a mismatch stress between polymer networks (e.g. softer vs. stiffer, swelling vs. non/less-swelling, hydrophobic vs. hydrophilic) for achieving different sensing actuations in response to various external stimuli. Moreover, the network structure of hydrogel sensors can be cross-linked using either irreversible or reversible crosslinkers/ additives⁴⁷⁻⁴⁸. Incorporation of single or multiple reversible crosslinkers/additives, in most cases, enable different components or regions of hydrogels to undergo different extents of volume expansion/contraction in certain positions, directions, or even swelling rates, thus leading to the programmable shape changes by bending, expanding, contracting, twisting, and fast buckling.

In all these designs, searching new responsive sensing materials/components and constructing well-defined network structures are equally important for the rational design of highly sensitive and robust hydrogel sensors. While it sounds simple and straightforward, the appropriate integration of sensing materials and entities into hydrogel networks still remains a challenge largely due to the incompatibility between materials, structures, and gelation methods. Moreover, on one hand, many hydrogel strain sensors exhibit the certain degree of reversible and multiple sensing ability due to their intrinsic stimuli-responsive nature; on the other hand, since the exposure of hydrogels to external stimuli often damages those irreversible bonds and crosslinkers in the hydrogels, hydrogel sensors also suffer from the loss of their original sensing ability. Thus, the introduction of self-healing functions in hydrogel sensors becomes necessary to rapidly recover the original network structure and to sustain their sensing ability through the dynamic reformation of reversible noncovalent interactions (e.g. hydrogen bonds, π - π stacking, hydrophobic interactions, host-guest interactions, and metal-coordination interactions) and/or reversible covalent bonds (e.g. imine bonds, disulfide bonds, acylhydrazone bonds, and boronate ester bonds)⁴⁹⁻⁵¹. Again, a cooperative and compatible fabrication of both self-healing and stimuli-responsive materials/entities in the same hydrogel may also face additional challenge. Similarly, hydrogel strain sensors must exhibit sensing-appropriate physical, mechanical, and biological properties. Generally, hydrogel strain sensors usually require high mechanical strength, toughness, and stretchability for transducing mechanical deformation into electrical/chemical/optical signals⁵²⁻⁵⁵. Specifically, *in vivo* injectable hydrogel strain sensors must be biodegradable and biocompatible, and their degraded products also need to be biocompatible with minimal inflammatory response.

All of these challenges from both materials and structural viewpoints highlight the importance of fabrication methods. Hydrogel strain sensors can be rationally

designed and fabricated from a large dataset of stimuli-responsive monomers and crosslinkers by different polymerization methods such as living cationic and anionic polymerization, reversible addition–fragmentation chain-transfer (RAFT) polymerizations, atom-transfer radical polymerization (ATRP), self-assembly, microfabrication, or laser writing, all of which can well control the chemistry and structure in hydrogel networks⁵⁶⁻⁶¹. In some cases, polymer networks in hydrogel sensors are readily functioned with different stimuli-responsive pendent groups or additives even before gelation, and resultant hydrogels can be directly used for sensing applications without the need of additional substrates or matrixes being served as sensor platform.

As shown in **Table 1** and **Figure 1**, we summarize and classify some classical hydrogel sensors with different types of sensing ability. This review aims to highlight the most important and recent works on hydrogel sensors in the past five years, instead a comprehensive one. Specifically, the review mainly covers the design principles and synthesis strategies of hydrogel sensors from both materials and structural viewpoints, selectively highlights some classical and interesting hydrogel sensors for different sensing purposes and applications, and finally presents some of the current scientific/technological barriers and the future research directions that should be undertaken to overcome these barriers.

Table 1. A summary and classification of different types of hydrogel strain sensors.

| Classify | Hydrogel | Signal | GF or LoD | Stretchability | Other | Reference |
|---------------------------------|--|-------------|--|----------------|---|--------------------|
| Conductive polymer-incorporated | PEDOT: PSS-polyAAm array | Electric | GF \approx 20 | \sim 15% | Long-term sensing (\sim 2 months), detect subtle force of 0.02~4.49N | Ref. ⁶² |
| | PANI-poly(AAm-co-HEMA) | Electric | GF=11 | \sim 300% | Detect wrist bending, speaking; biocompatible | Ref. ³⁹ |
| | PANI/PSS-UPyMA | Electric | GF=3.4 | \sim 300% | Self-healing (<30 s); detect pulse beating, speaking, finger bending | Ref. ⁶³ |
| | polyNIPAAm/PANI | Electric | GF=3.92 | \sim 200% | Stable performance (\sim 350 cycles) | Ref. ⁶⁴ |
| Polyelectrolyte-incorporated | ACC-polyAAc/Sodium Alginate (SA) | Capacitance | LoD \approx 1k Pa | \sim 55% | Self-healing; detect speaking, blood pressure, and finger bending | Ref. ⁶⁵ |
| | Poly(MAA-co-DMAPS) | Electric | LoD=0.6~0.7% ^{$^{\circ}\text{C}^{-1}$} | >10000% | Self-healing; Temperature-responsive sensor (10~80 $^{\circ}\text{C}$) | Ref. ⁶⁶ |
| Nanoparticles-incorporated | Chitosan-AuNPs | Color | LoD=2.4 μM of H_2O_2 | / | Wide detection range (8.0 μM -15 mM) | Ref. ⁶⁷ |
| | PNIPAM-AuNPs | Color | LoD=0.2 $^{\circ}\text{C}$ | >100% | Color-temperature sensor range (25~40 $^{\circ}\text{C}$); detecting time (\sim 1s) | Ref. ⁶⁸ |
| | Fe ₃ O ₄ -poly(AAc-co-AAm) | Magnetic | LoD=0.1 pH unit | / | Repeatable, reversible detection; detecting time (<60 min) | Ref. ⁶⁹ |
| | Platinum nanoparticles (PtNPs)-PANI array | Electric | LoD \approx 0.2 mM of glucose | / | High selectivity; signal-to-noise ratio of \sim 3 | Ref. ⁷⁰ |

| | | | | | | |
|------------------------------------|---|-------------|------------------------------------|--------------|--|--------------------|
| | PtNPs-PANI | Electric | LoD= \sim 0.7 μ M of glucose | / | High selectivity; detecting time (<3 s) | Ref. ⁷¹ |
| | AgNWs-polyAAm | Electric | GF=0.71 | >22000% | Wide working condition (-20 \sim 80 $^{\circ}$ C); detect breathing, speaking, and finger bending | Ref. ⁷² |
| | Nano barium ferrite (BaFe ₁₂ O ₁₉)-polyAAc | Electric | / | >40% | High ionic conductivity (1.22×10^{-2} S cm ⁻¹); good self-recoverability | Ref. ⁷³ |
| | PDA-CNTs-poly(AAc-AAm) | Electric | / | \sim 700% | Self-adhesive; wide working condition (-20 \sim 60 $^{\circ}$ C); detect arm bending and wrist pulse | Ref. ⁷⁴ |
| | MXene (Ti ₃ AlC ₂)-polyvinyl alcohol (PVA) | Electric | GF=25 | >3400% | Self-healing; self-adhesive; detect human speaking, writing, and smiling | Ref. ⁷⁵ |
| | PC/rGO-PVA | Electric | GF=14.14 | >5000% | Self-healing (\sim 3s); detect finger bending, smiling, speaking, and wrist pulse | Ref. ⁷⁶ |
| | F-SWCNT-polyPDA-PVA | Electric | / | >100% | Self-healing; self-adhesive; detect bending and relaxing of walking, chewing, and pulse | Ref. ⁷⁷ |
| | SWCNT/PVA | Electric | GF=1.51 | >1000% | Self-healing; detect bending and relaxing of knee/finger (>1000 cycles) | Ref. ⁷⁸ |
| | TA/sodium alginate (SA)-polyAAm | Electric | GF=2.0 | >2100% | Self-healing; detect smiling, finger bending, and wrist pulse | Ref. ⁷⁹ |
| | KCl-(κ -carrageenan)/polyAAm | Electric | GF=0.63 | \sim 1000% | Self-healing; detect finger bending | Ref. ⁸⁰ |
| | Cu ²⁺ -polyAAm | Electric | LoD= \sim 0.005% Strain | >1500% | Detect finger bending, speaking, and wrist pulse | Ref. ⁸¹ |
| | NaCl-gelatin/PVA | Electric | GF= \sim 0.4 | \sim 715% | Lower working condition (-20 $^{\circ}$ C); detect finger and elbow bending, speaking | Ref. ⁸² |
| | LiCl-poly(Acrylated thymine-AAm) | Electric | / | \sim 2000% | Self-healing; self-adhesive; detect breathing, speaking and finger bending | Ref. ⁸³ |
| Inorganic electrolyte-incorporated | NaCl-polyAAm | Capacitance | / | >590% | Detect finger bending (>4000 cycles) and location of touch | Ref. ⁸⁴ |
| | LiCl-polyAAm | Capacitance | / | >1000% | Detect location of touch (work as smart screen) | Ref. ⁸⁵ |
| | NaCl-SA/ polyAAm | Electric | GF=2.0 | \sim 3120% | Detect speaking, finger bending, and wrist pulse | Ref. ⁸⁶ |
| | NaCl/SDS-regenerated silk fibroin(RSF)/HPAAm | Electric | GF=2.0 | >1900% | Detect finger bending and location of touch | Ref. ⁸⁷ |
| | LiCl-polyAAm | Capacitance | GF=4.0 | >500% | Adhesive; Stable performance (over 1500 cycles) | Ref. ⁸⁸ |
| | PIL-BF ₄ /PEDGA | Electric | / | >1400% | Wide working condition (-75 $^{\circ}$ C to 340 $^{\circ}$ C); detect finger bending (>10000 fatigue cycles) | Ref. ⁸⁹ |
| Biomolecule-incorporate | PVA/RSF/borax | Electric | / | \sim 5000% | Track leg, knee bending and different gestures | Ref. ⁹⁰ |

| | | | | | | |
|---|----------------------|-------|-----------------------|---|-------------------------------------|--------------------|
| d | Poly(AAm-co-aptamer) | Color | LoD=0.0128HAU of H5N1 | / | <30 min detection time | Ref. ⁹¹ |
| | DNA-based | Cell | / | / | Detect live circulating tumor cells | Ref. ⁹² |

Note: Gauge Factor (GF); Limit of Detection (LoD).

2. General Design Strategy and Categories of Hydrogel Strain Sensors

To better understand the structure-function relationship of hydrogel strain sensors, here we classified hydrogel strain sensors into five basic groups of nanoparticle-incorporated, conducting polymer-incorporated, polyelectrolyte-incorporated, inorganic salt-incorporated hydrogel, and biomolecule-incorporated hydrogel strain sensors, mainly depending on structural-dependent network structures, gelation methods, and sensing mechanisms, not depending on the nature of the stimuli. Since the five types of hydrogel strain sensors possess anisotropic structures, a general working principle is to create non-uniform spatial stresses in different regions/parts of the hydrogels to realize different stimuli-responsive sensing properties via strain-induced shape-adaptive actuations. On the other hand, while the five types of hydrogel strain sensors can achieve the similar or same stimuli-responsive sensing capacity (i.e. thermo, light, electric, and pH sensing capacity)⁹³, they are driven by different sensing mechanisms strongly depending on their network structures (**Figure 1**). The inorganic nanofillers-incorporated hydrogel sensors are constructed by adding nanofillers or crosslinkers in polymer networks to create hybrid polymer/inorganic structures where both materials contribute unique and beneficial properties to hydrogel sensors, while the latter hydrogel sensors are likely constructed by different polymers to create an overall heterogeneous polymer/polymer structures. All these network structures allow to create and maximize the stress mismatch for strain-induced actuation upon external stimuli, and such sensing mechanics of these hydrogel sensors can further be tuned and optimized by changing the compositions in hydrogel matrix, tailoring to specific applications.

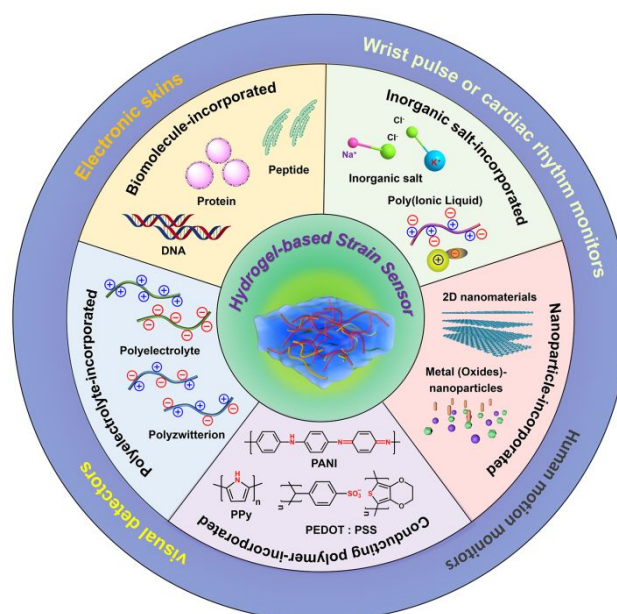


Figure 1. Overview of five typical types of hydrogel strain sensors.

2.1. Nanoparticle-incorporated hydrogel sensors

Due to the unique and superior optical, conductive, and magnetic properties of

nanoparticles (NPs), physical incorporation or chemical crosslinking of nanoparticles into polymer network enables to construct hybrid inorganic NPs/polymer network structures, which help to translate the conformational change of the surface bound stimuli-responsive polymers into observable optical property changes and improve mechanical property, making them as promising materials for the desirable sensing applications^{72-73, 76, 94}. A number of the widely used one/two/three-dimensional NPs of gold nanoparticles (AuNPs), gold nanorods (AuNRs), silver nanoparticle (AgNPs), carbon nanotubes, graphene oxide, and MXenes, and magnetic nanoparticles (Fe_3O_4) have been incorporated into polyAAm, polyNIPAM, PVA, poly(NIPAM-*co*-AAm), and poly(AAc-*co*-AAm) to produce several representative strain sensors of pH, temperature, color and human movements⁹⁵. As a typical example, AuNPs are often incorporated into a hydrogel matrix containing -SH, -CN or -NH₂ groups via the formation of dynamic covalent bonds, which are responsive to different stimuli in different strain sensors. AuNPs can be readily self-assembled on amine-rich chitosan hydrogel matrix through horseradish peroxidase (HRP) immobilization, producing AuNPs-incorporated hydrogel biosensor⁶⁷, which showed a wide range of response to H₂O₂ (8.0~15 μM), a lower detection limit of 2.4 μM , and long-term sensing stability up to 4 weeks. Moreover, AuNPs can also be modified by plasmonic nanostructures with different plasmonic materials, cluster structures, and geometries, and the modified AuNPs are used as real-time colorimetric indicators for hydrogel color sensors. As shown in **Figure 2a**, combining of plasmonic AuNPs with thermo-responsive polyNIPAM hydrogels, a smart colorimetric stretchable hydrogel biosensor was able to achieve rapid, reversible, and strain-insensitive color shifts between red and grayish violet in response to a temperature change from 25 °C~40 °C within 1 s⁶⁸. Apart from conventional AuNPs, AgNPs, and plasmonic nanoparticles, the incorporation of magnetic Fe_3O_4 nanoparticles into poly(AAc-*co*-AAm) hydrogels enabled to produce a pH sensor, which displayed a repeatable and reversible response to the pH change, with a sufficient sensitivity to detect 0.1 unit change in pH (**Figure 2b**).⁶⁹

Carbon nanotubes (CNTs) and reduced graphene oxide (rGO) as typical two-dimensional carbon materials have been widely integrated into and used as different electronic sensing devices made of elastomers, polymers, and organics due to their superior electronic properties of Fermi velocity, thermal conductivity, charge carrier mobility, and mechanical strength⁹⁶⁻⁹⁹. But, strong hydrophobicity and poor solubility of CNTs and rGO make it very challenging to directly incorporate them into highly hydrophilic hydrogels (70-90% water content) and to avoid their aggregation in hydrogel matrix, while still retaining their electronic sensing functions. To overcome this issue, a common strategy is to modify these hydrophobic carbon materials with hydrophilic/charge phenol hydroxyl, carboxylic acid, epoxide, and oxide groups to not only improve the dispersion of CNTs and strengthen interfacial interactions with polymer network, but also enhance mechanical and electrical properties via electrostatic and π - π interactions, hydrogen bonding. Consequently, different modified CNTs have been incorporated into polyAAm, polyAAc, polysaccharides, gelatin, collagen, and polyethylene glycol (PEG) hydrogels via hydrothermal and solvothermal reactions, cross-linking gelation, doping methods, and template-based synthesis. Among different CNTs-incorporated hydrogel strain sensors, flexible and wearable strain sensors become immense importance for ultrasensitive human-machine interaction, healthcare monitoring, and human motions. As a classical example, conductive functionalized single-wall carbon nanotube (FSWCNT), biocompatible polyvinyl alcohol (PVA), and polydopamine (PDA) were crosslinked to form a healable and adhesive PVA-

FSWCNT-PDA hydrogel with dynamic supramolecular structures, which exhibited fast self-healing ability (within 2 s), high self-healing efficiency (99%), and robust surface adhesion on different substrates (**Figure 2c**). PVA-FSWCNT-PDA hydrogel was further fabricated into a wearable soft strain sensor for real-time detection of different human motions of finger bending and relaxing, walking, chewing, and pulse (**Figure 2d**).⁷⁷ To expand this idea, single wall carbon nanotube (SWCNT), GO, and silver nanowire (AgNWs) were separately incorporated into PVA hydrogels to produce different types of NPs/PVA hydrogels as conductive strain sensors, all of which achieve fast and high self-healing efficiency (98%) of electric signals within ~ 3 s, sustain extreme elastic strain of 1000% with a gauge factor of 1.51, and effectively monitor and distinguish multifarious human motion of finger, elbow, knee, and neck.⁷⁸ More impressively, MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) as another 2D carbonitrides/metal carbides was incorporated into PVA hydrogel to MXene-based hydrogel strain sensor, which can detect various bodily motions (hand gestures and facial expressions) and to monitor vital signals (human pulse and vocal sound) (**Figure 2e**).⁷⁵ Such high strain-induced electromechanical sensitivity is largely attributed to the 3D network structure of the MXene nanosheets embedded within the hydrogel matrix. Large deformation reduces the spacing between the nanosheets, yet increase surface contacts between MXene nanosheets, transform face-to-edge interconnections into face-to-face interconnections, all of which decrease M-hydrogel resistance and thus increase detection sensitivity. We should note that except for the above-mentioned examples, most of nanoparticle/polymer hydrogel strain sensors can only be stretched to a strain of $\sim 200\%$, thus the breaking of conducting contacts during deformation usually leads to the poor and irreversible detection sensitivity of these strain sensors. Additional efforts should be made to increase the stretchability and self-healing properties of these nanoparticle/polymer hydrogel strain sensors.

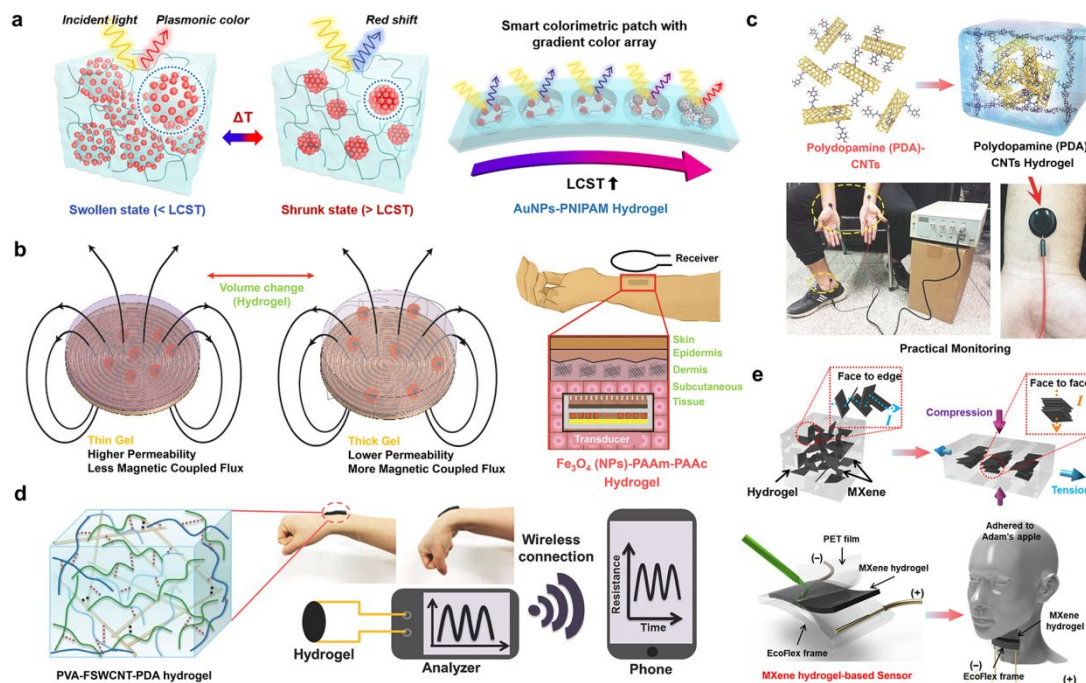


Figure 2. Nanoparticle/polymer hydrogel sensors. (a) Thermo-responsive colorimetric plasmonic AuNPs-PNIPAM hydrogel sensors, enabling to exhibit rapid and reversible color shifts from red to violet in response to a temperature change (25–40 °C) within 1 s. [Adapted with permission from (⁶⁸), copyright 2018 Nature Publishing Group]. (b)

Wireless iron oxide nanoparticle (Fe_3O_4 NPs)-embedded poly(AAc-co-AAm) hydrogel sensors that can detect subtle pH changes (0.1 unit) in response to a magnetic field. [Adapted with permission from (69), copyright 2014 Elsevier]. (c) Mussel-inspired PDA-CNTs-incorporated poly(AAm-AAc) hydrogels with highly adhesive, tough, and conductive properties for detecting human wrist pulse even under $-20\text{ }^\circ\text{C}$. [Adapted with permission from (74), copyright 2018 Wiley-VCH]. (d) Automatable healable and adhesive PVA-FSWCNT-PDA hydrogel strain sensor for real-time detection of human motions of finger bending and relaxing, walking, chewing, and pulse with fast self-healing ability (within 2 s) in response to external changes of stress or strain⁷⁷. (e) MXene-PVA hydrogel sensors for monitoring electromechanical signal changes with a gauge factor of 25. [Adapted with permission from (75), copyright 2018 American Association for the Advancement of Science].

2.2. Conducting polymer-incorporated hydrogel strain sensors

Conducting polymers such as polypyrrole (PPy), polyaniline (PANI), and poly(3, 4-ethylene-dioxythiophene) (PEDOT) are π -conjugated polymers with alternating single and double covalent bonds for conducting electrons¹⁰⁰⁻¹⁰². Use of conducting polymers to make hydrogel strain sensors possesses several intrinsic advantages: (1) conductive polymers themselves are able to carry solvent ions for electrical conduction with fairly low resistance in the hydrogel networks; (2) as opposite to rigid NPs and metallic additives in polymer hydrogels to empower electronic conductivity, conductive polymer chains are very flexible and compatible with other polymers in the same hydrogel systems for empowering their high stretchability. Less structural disparity in network length scales can reduce the source of inhomogeneity in mechanical and electrical properties; (3) obviously, conductive polymers can be simply fabricated with other elastomeric and polymer substrates into electronic sensors, so that conjugated polymers inside hydrogel networks possess high conductivity and thermal stability for piezoresistive strain sensors^{64, 103-105}.

A general working mechanism for conducting hydrogel strain sensors is the delocalization of π -bonded electrons over the conjugated backbone structures. To this end, PANI, as firstly described in the mid-19th century by Henry Letheby, has been widely used for hydrogel bioelectronics¹⁰⁶⁻¹⁰⁷. As an interesting example, a triplex biosensor made of nano-patterned PANI hydrogels and different enzymes were able to detect triglycerides, lactate, and glucose, with good selectivity and high sensitivity in both PBS and human serum samples.⁷⁰ The hydrophilic porous microstructure of the PANI hydrogel was favorable for the transportation of electrons generated from hydrogen peroxide in the enzymatic reactions. To enhance the electronic conductivity of hydrogel strain sensors, another common design strategy is to integrate conducting polymers with various ionic or organic dopants and nanoparticles. The incorporation of such dopants enables to not only create free radicals that can pair with the dopant to form polarons, but also oxidize (p-doping) or reduces (n-doping) the conducting polymer at the π -bond sites by removing or donating electrons, both of which offer additional paths for charge carriers along with the conducting polymer backbone¹⁰⁸. Following this working principle, the incorporation of platinum nanoparticles (PtNPs) into PANI hydrogel allowed to construct a glucose sensor, with a ultrahigh low detection limit of $0.7\text{ }\mu\text{M}$ glucose with 3 s (**Figure 3a**).⁷¹ The significant increase of glucose detection ability of PtNPs/PANI hydrogel sensors is attributed to enhance electrocatalytic activity for oxidizing H_2O_2 . Similarly, polyAAm hydrogel doped with poly(3, 4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT: PSS) conductive

polymers create a classical piezoresistive tactile sensor (**Figure 3b**).⁶² However, additional challenge still remains. Simple doping/mixing of additives into conductive polymer network usually does not necessarily to enhance mechanical strength, instead make the hydrogels become more brittle due to over-crosslinking effect.⁶³ To address this issue, the rational design of interpenetrating network (IPN) between conducting polymers and other polymers is a possible solution to minimize potential trade-offs between mechanical and electrical properties via in situ polymerization or in-growth polymerization. Using this design strategy, a number of conducting hydrogels with IPN have been developed by polymerizing conducting polymers (e.g., PEDOT: PSS and PANI) with other polymers (e.g. polyAAm, polyAAc, and gellan gum)). All of these conductive IPN hydrogel sensors displayed the enhanced mechanical properties as compared to conductive hydrogel sensors without IPN, while still retaining high sensing ability (e.g. gauge factor=11) (**Figure 3c**).³⁹ Moreover, considering that double-network (DN) structure is a special case of IPN, several recent attempts have fabricated the two different polymers to form conductive hydrogels with DN structure for imparting both high electronic conductivity and mechanical toughness, including PEDOT: PSS/PDMAAm DN hydrogels¹⁰⁹ and polyAAc/PEDOT: PSS DN hydrogel¹¹⁰.

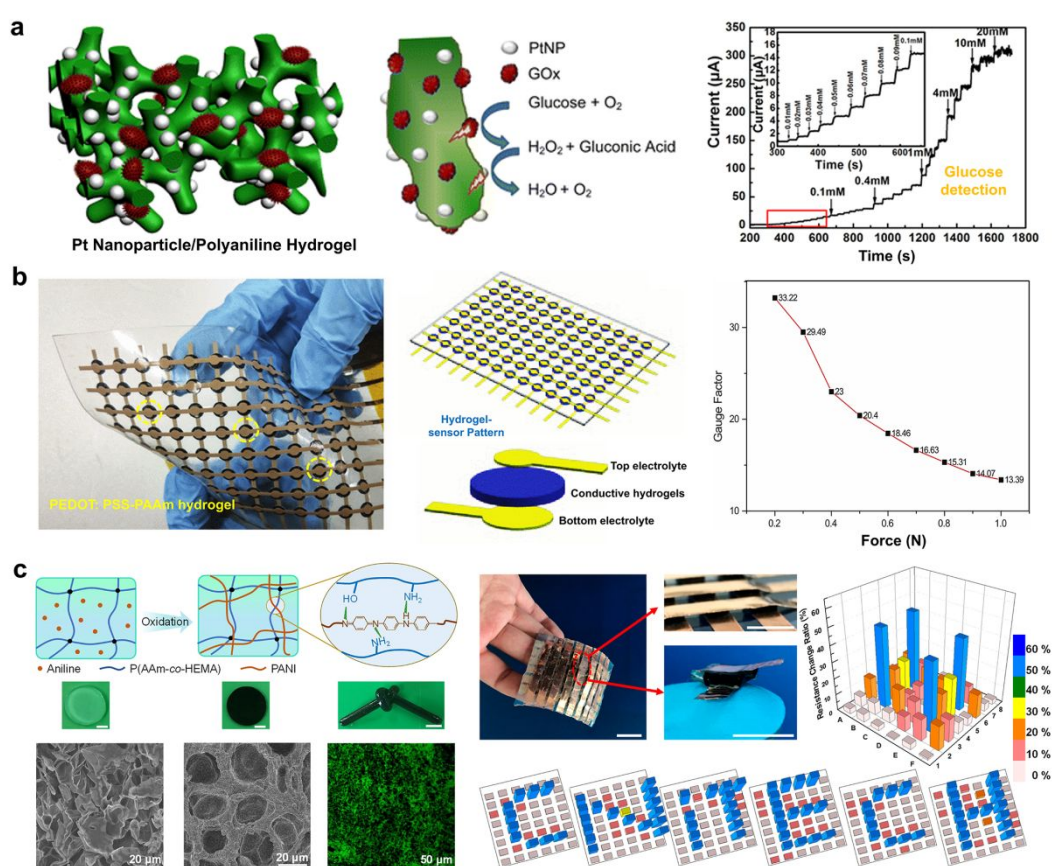


Figure 3. Conductive polymer hydrogel strain sensors. (a) PtNPs/PANI hydrogels as a glucose sensor with high sensitivity of $96 \mu\text{A} \cdot \text{mM}^{-1} \cdot \text{cm}^{-2}$, low detection limit of $0.7 \mu\text{M}$, and fast response time of ~ 3 s. Such unprecedented sensitivity is largely attributed to synergistic integration of PtNPs catalysts into 3D-microstructured PANI hydrogel matrix for promoting the electro-oxidation of hydrogen peroxide. [Adapted with permission from (71), copyright 2013 American Chemical Society]. (b) PolyAAm/PEDOT:PSS piezoresistive hydrogel sensors with high gauge factor of

13~33 in response to subtle force of 0.2~1.0 N. The blending of PEDOT: PSS into PAM hydrogels allows to reduce output impedance ($k\Omega$) so as to promote piezoresistive sensitivity. [Adapted with permission from (62), copyright 2018 IEEE. (c) Conductive PANI-poly(AAm-co-HEMA) hydrogel sensors with high sensitivity ($GF = 11$) at low strain and outstanding linearity at high strains for detecting human motions of speaking, wrist pulse, and hand writing. [Adapted with permission from (39), copyright 2018 American Chemical Society].

2.3. Polyelectrolyte-incorporated hydrogel strain sensors

Polyelectrolytes (e.g. poly(2-acrylamido-2-methylpropane-1-sulfonic acid) [poly(AMPS)], polyAAc, polyzwitterions) are among the most studied macro-ionic molecular systems. Considering the ionic nature of polyelectrolytes, polyelectrolyte hydrogels by copolymerizing these electrolyte monomers into hydrogel networks possess intrinsic ionic groups and the counterions, thus they commonly undergo a volume shrinking or swelling in response to pH and ionic changes¹¹¹⁻¹¹³. As compared to neutral polymer hydrogels, polyelectrolyte hydrogels usually exhibit “polyelectrolyte effect” behavior, i.e. polyelectrolyte chains undergo a fully stretching (swelling) conformation in water, but adopt a collapsed (shrinking) conformation into salt solution, simply because the introduction of polyelectrolytes will screen out long-range electrostatic repulsions and short-range excluded volume interactions between and within polyelectrolyte chains, leading to ion/pH-responsive volume changes¹¹⁴⁻¹¹⁵. Moreover, strong binding of counterions to polyelectrolyte chains creates additional crosslinks in hydrogel network, which influences mechanical properties of polyelectrolyte hydrogels and even causes gel collapse in some cases. Moreover, the presence of the charged groups allows to introduce metal ion coordination and supramolecular interactions in hydrogel networks and thus to promote the hydroelectricity separation and conductivity of the hydrogels.

Copolymerization of charged monomers [e.g. AMPS, AAc, 2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl) ammonium hydroxide (SBMA), 3-dimethyl (methacryloyloxyethyl) ammonium propanesulfonate (DMAPS)] with neutral acrylamide monomers [e.g. AAm, NIPAM, HEMA]^{66, 116-118} and introduction of these charged monomers into hydrogel network (e.g. PVA, P2VP, SA or polyAAm) to form IPN structures¹¹⁹⁻¹²³ are two common strategies to construct polyelectrolyte hydrogel sensors. The copolymerization strategy can achieve poly(SBMA-co-HEMA) hydrogel sensor polyelectrolyte hydrogels with high fracture elongation of 2000~10000 %, fracture strength of 0.2~0.6 MPa, and gauge factor of more than 1.5 (**Figure 4a**). Another zwitterionic poly(MAA-co-DMAPS) hydrogel sensors with UCST and LCST characteristics display ultrastretchability up to 10000%, which can converse forces to electrical signals for tracking human movements and perceiving changes in external temperature (**Figure 4b**)⁶⁶. IPN structures can slightly enhance the tensile strength or sensitivity of hydrogel sensors by improving the integrity of network structures. For instance, polyAAc/SA, polyAAc/PAAm, polySBMA/PVA strain sensors exhibited 300~1000% of stretchability, ~0.6 MPa of tensile strength, and high detection capacity for multiple-time elbow/finger bending. Moreover, polyAAc/SA hydrogel sensors also exhibited high and sustainable sensitivity for detecting a wide range of pressures between 0.17~1000 kPa (**Figure 4c**).⁶⁵

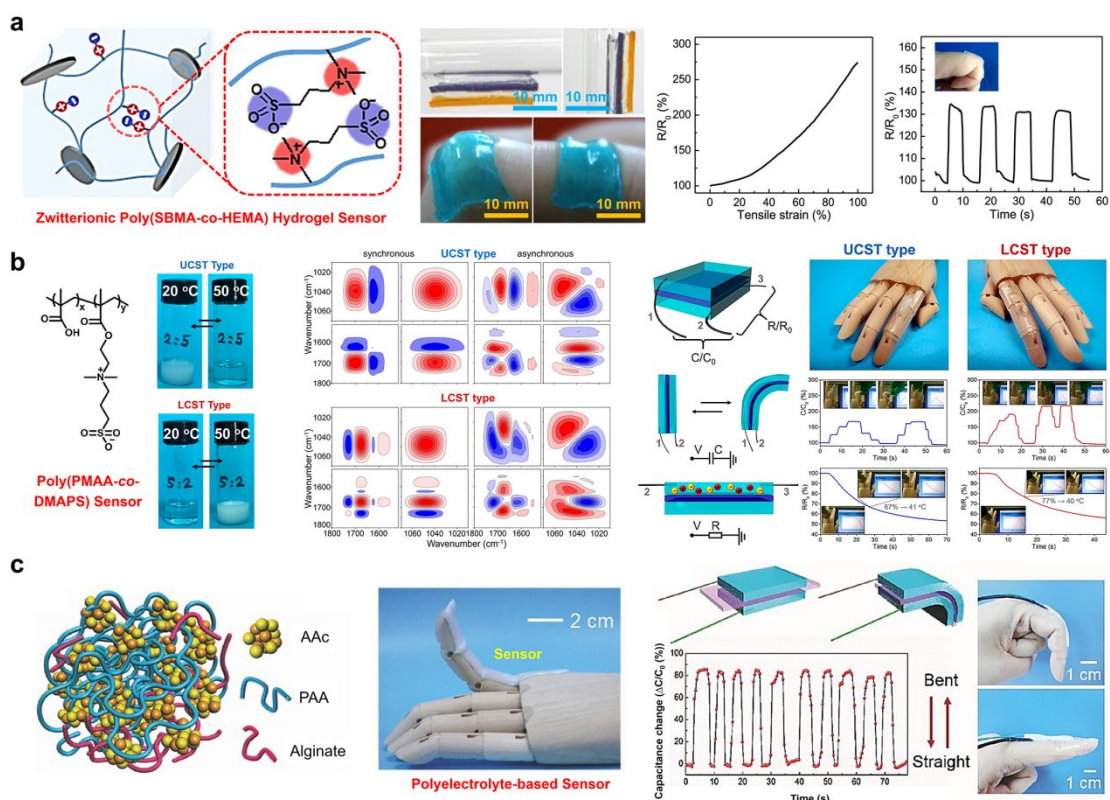


Figure 4. Polyelectrolyte-incorporated hydrogel strain sensors. (a) Poly(SBMA-*co*-HEMA) hydrogel sensors with high strain conductivity and sensitivity (gauge factor=1.8), high fracture toughness of 2.45 MJ m^{-3} , fracture strain of 2000%, fracture strength of 0.27 MPa, and compliant adhesion on different surfaces (hydrogels, skin, glasses, silicone rubbers, and nitrile rubbers) [Adapted with permission from ⁽¹¹⁶⁾, copyright 2019 American Chemical Society]. (b) Zwitterionic poly(MAA-*co*-DMAPS) hydrogel sensors to detect the movements of the wooden prosthetic finger and environmental temperature changes by tuning UCST and LCST for converting forces to electrical signals. [Adapted with permission from ⁽⁶⁶⁾, copyright 2018 American Chemical Society]. (c) PolyAAc/SA hydrogels used as skin-mimic sensors for detecting subtle pressure changes as induced by a gentle finger touch, human motion, or small water droplets. [Adapted with permission from ⁽⁶⁵⁾, copyright 2017 Wiley-VCH].

2.4. Inorganic salt-incorporated hydrogel strain sensors

Different from polyelectrolyte hydrogel strain sensors, electrolyte hydrogels are typically prepared by direct physical or chemical doping of sodium chloride (NaCl), lithium chloride (LiCl), and cupric ion (Cu^{2+}) into polyAAM, HPAAM, and PVA hydrogels. Direct physical doping of NaCl, LiCl, and Cu^{2+} salts into polyacrylamide (polyAAM) hydrogels provide a simple and straightforward route to form ion-doped electrolyte hydrogels.⁸⁴⁻⁸⁵ The resultant NaCl/polyAAM, LiCl/polyAAM, Cu^{2+} /polyAAM hydrogel strain sensors are not only highly stretchable up to 15-times in their original length and stable to sustain over 1000 pressure-capacitance cycles, but also detect any subtle human motion such as smiling, speaking, and finger bending. Moreover, such electrolyte hydrogels can also be fabricated into epidermal touch panel used as human skin-machine interfaces for writing words, and playing games and piano. (**Figure 5a**). To enhance mechanical property, doping of different salts in DN network structure has produced different hydrogel strain sensors, including (i) κ -

carrageenan/polyAAM DN hydrogel doped with KCl to achieve a great strain sensitivity with a gauge factor of 0.63 at the strain of 1000%, elastic modulus of 280 kPa, and a fracture energy of 6150 J/m².⁸⁰; (ii) PVA/ gelatin doped with NaCl to achieve fracture stress of 1 MPa, fracture strain of 715%, elastic modulus of 157 kPa, and toughness of 3605 kJ/m³;⁸² (iii) SA/tannic acid (TA)/polyAAM hydrogel with ternary ionic multibond network with high sensitivity (GF of 2.0) (**Figure 5b**)⁷⁹. All of these salt-doped hydrogels were fabricated into stretchable wearable strain sensors for real-time monitoring of various human motions and physiological signals. While physical doping could achieve the regeneration of electrical conductivity by simple re-soaking methods, strong dependence of salt concentrations on ion-doped polyelectrolyte hydrogels would also affect the sensitivity and specificity of hydrogel sensors in real-world applications.

Different from direct physical doping, chemical doping strategy helps to enhance mechanical property of hydrogels. Usually, chemical doping strategy drives free salt ions to strongly bind to polymer network via metallic ion coordination and supramolecular assembly. Such interactions reduce the possibility of salting-out phenomena and blockage of the network channels of hydrogel sensors, both of which would cause the failure of hydrogel sensors. Chemical doping of sodium dodecyl sulfate (SDS)/NaCl into polyAAM or HPAAM hydrogel network containing sodium alginate (SA) nanofibrillar, regenerated silk fibroin (RSF), and cellulose derivatives allows to improve mechanical properties. NaCl/SA/polyAAM⁸⁶ and NaCl/SDS-RSF/HPAAM⁸⁷ hydrogel sensors (0.65-1.2 MPa) possessed 2~7 times higher tensile stress than pristine hydrogel sensors (0.1-0.2 MPa), with maximum stretchability up to 1800%~3100%. For NaCl/SDS-RSF/HPAAM DN gel (**Figure 5c**), SDS not only promoted the rapid formation of the first SDS-RSF network, but also forms SDS micelles to act as cross-linked points for second HPAAM network. All of these tough electrolyte hydrogels can also be used as touchable or resistance-sensitive devices for sensing electronic signals.

Ionic liquids (ILs) are composed of cation-anion pairs of an organic ion and inorganic counterion. Different from those inorganic salts, ILs are hydrophobic and difficult to add into hydrophilic hydrogels directly. Using click reaction and solvent exclusion methods, PIL-BF₄⁸⁹, 1-butyl-3-methylimidazolium chloride (BMIMCl)¹²⁴, and [C16mim]⁺Cl⁻¹²⁵ were encased or cross-linked into PEDGA/PETA, xanthan gum, bulk g-C₃N₄ hydrogels. The resultant hydrogel sensors possessed high tensile strength of 1.5~2.2 MPa, stretchability of 1500% up to 10000 fatigue cycles, and broad thermal responsive range of -75 °C~340 °C. Due to the high ionic conductivity (0.83 S m⁻¹ at room temperature), hydrogel sensors can retain their high and stable electric sensitivity even at extremely low (-60 °C) or high (200 °C) temperature (**Figure 5d**). Furthermore, ILs are promising for preparing anti-freezing organogel or hydrogel sensors, which require further research efforts in this aspect.

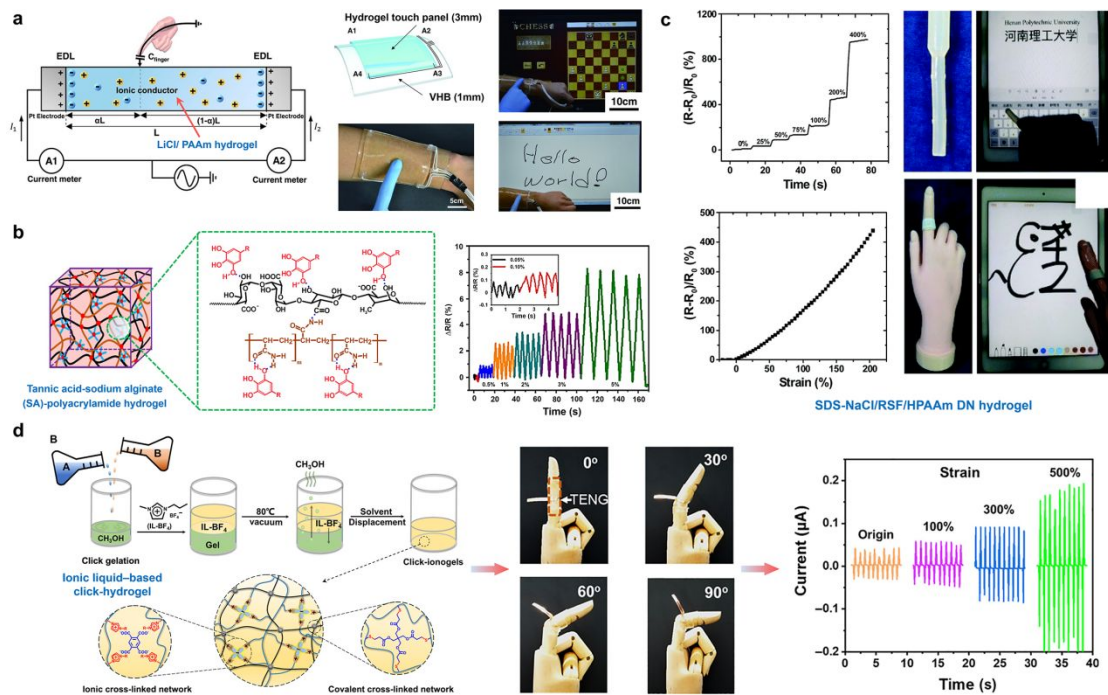


Figure 5. Inorganic salt-incorporated hydrogel strain sensors. (a) LiCl-polyAAM hydrogel sensor with high stretchability and transmittance, which is further used as ionic touch panel for writing words and playing games and piano. [Adapted with permission from (85), copyright 2016 American Association for the Advancement of Science]. (b) SA/TA/polyAAM hydrogel sensor with a high gauge factor of 2-9 at a subtle (<100%) and large (2100%) strains for monitoring large limb motions of the human body (finger, knee, and elbow) and subtle muscle movements (smiling, chewing, and wrist pulse). Adapted with permission from (79), copyright 2019 American Chemical Society]. (c) NaCl/SDS-RSF/HPAAm hydrogel sensor with high compression/tensile strength of 122/1.2 MPa, large extensibility of 19, high toughness of 1769 J/m², and high ionic conductivity of 0.012 S/cm. High ionic conductivity and strain sensitivity enable the RSF/HPAAm DN gel to be used as touching screen pen and electronic skin. [Adapted with permission from (87), copyright 2019 Royal Society of Chemistry]. (d) Ionic liquid-based PIL-BF₄/PEDGA hydrogel strain sensor with high ionic conductivity (0.83 S m⁻¹ at room temperature) for detecting finger bending under wide temperature range (-75 °C~340 °C) over 10,000 fatigue cycles. [Adapted with permission from (89), copyright 2019 American Association for the Advancement of Science].

2.5. Biomolecule-incorporated hydrogel strain sensors

Hydrogels integrating with biomolecules (e.g. proteins, peptides, antibody, DNAs, enzymes) presents many general bio-related advantages of biodegradability, biocompatibility, and biostability, as well as specific bio-functionalities of drug/gene carriers, bioactivity, and bioimaging¹²⁶⁻¹²⁸. From a fabrication viewpoint, biomolecule-based hydrogels are often fabricated via a variety of methods, including click chemistry, Michael addition of cysteine residues to vinyl sulfones or maleimides, UV-initiated cross-linking, native chemical ligation, nonspecific amine-carboxylic acid couplings, and self-assembly¹²⁹⁻¹³¹. Functionally, biomolecule-based hydrogels achieve their specific functions via simple sequence design, but stimuli-responsive sensing properties from the coupling of functional biomolecules with the physical properties of polymers. Incorporation of biomolecules into synthetic polymer networks also could influence the

swelling, structure, and mechanical properties of the hydrogels. Practically, most of biomolecule-based hydrogels are dominantly used for tissue engineering and extracellular matrix (ECM) mimics, but stimuli-responsive biomolecule-based hydrogels have attracted increasing interests for the next-generation bioelectronic interfaces over the last decade, due to their similarities to biological tissues and versatility in electrical, mechanical, and biofunctional engineering.

For protein/polymer hydrogels formed by native proteins (e.g. collagen, gelatin, silk fibroin, bovine serum albumin, β -lactoglobulin, YajC-CT, and ovalbumin) and synthetic polymers, they achieve stimuli-responsive properties mainly through conformational changes between native and denaturation states upon external simulation¹³². For example, a series of PEG/protein hydrogels were synthesized with different proteins of soy protein, hydrolyzed soy protein, pea albumin, and casein¹³³⁻¹³⁵. Due to polyelectrolyte nature of the proteins, the resultant PEG/protein hydrogels exhibited pH responsiveness of drug release, but mechanical properties of these hydrogels were still weak. Apart from PEG, other polymers including PVA, poly(propylene oxide) (PPO), polyAAc, and polyHEMA have been used to fabricate with RSF to produce polymer/RSF hybrid hydrogels, which can be regulated by heating, variation of pH¹³⁶, alcohol, ions⁹⁰, and shearing. RSF usually adopts β -sheet structures and favors to aggregate these β -sheets into crystalline fibrous structures in polymer networks, and such hierarchical structures are main contribution to the excellent mechanical property of polymer/RSF hybrid hydrogels. Some PVA/RSF/borax hydrogel can also be used as a physical sensor to detect the bending and release of the leg, hand, and finger (**Figure 6a**). However, the low stability and ease denaturation of proteins make protein/polymer hydrogels vulnerable for their sensing, mechanical, and biological properties. As an alternative, small peptides can mimic main function of natural proteins, be facile synthesized and precise modified by simply controlling their sequences at large-scale and low-cost level via gene expression in bacteria, recombinant technology, and solid-phase peptide synthesis, and be easily incorporated with polymers via the click chemistry. One design strategy to introduce stimuli-responsive properties for these peptides is to control their conformational changes via sol-to-gel transition by various environmental stimuli. For instance, FEFEFKFK/polyNIPAAm and POG8/PEG hydrogel exhibited thermo-responsive properties that can be tuned by self-assemble of FEFEFKFK into β -sheet-rich fibers and POG8 into triple-helix fibers¹³⁷⁻¹³⁸.

Compared to proteins and peptides, DNA possesses enhanced stability under intensive heating, pressure, and chemical processing. DNA-functionalized hydrogels are still a relatively new field. The most important property of DNA hydrogel is that nucleobases including adenine (A), thymine (T), guanine (G), cytosine (C), and uracil (U) serve as programmable microscopic motifs or crosslinkers for constructing predictable secondary structural network from bottom up via the base-pairing hybridization¹³⁹. The hybridization of complementary DNA strands leads to the crosslinking of polymer chains and hydrogel formation with precise structural control and specific responses. DNA generally behaves like a long linear polymer and forms a hydrogel via physical entanglement or by chemical crosslinking of other polymers, composites, and small molecules. As nucleobases was independently introduced into polyacrylamide, DNA-polyAAm hydrogels can greatly enhance their elastic modulus of 0.43 MPa by several orders of magnitude¹⁴⁰, as well as surface adhesion (220-780 N/m) on various solid materials, including polytetrafluoroethylene, plastics, glasses,

rubbers, metals, and woods.¹⁴¹ Such mechanical enhancement in DNA (linear)-polyacrylamide hydrogels is largely attributed to their DNA-self-assembled supramolecular structures. Apart from linear DNAs, DNA can also be precisely designed and self-assembled into different branched architectures of X, Y, T, cross-shapes, which were further self-assembled into large-scale, three-dimensional hydrogel structure via efficient, ligase-mediated reactions, but such branched DNA hydrogels were very weak with tensile modulus of 1-50 KPa and tensile strain of 0.42-0.57¹³⁹.

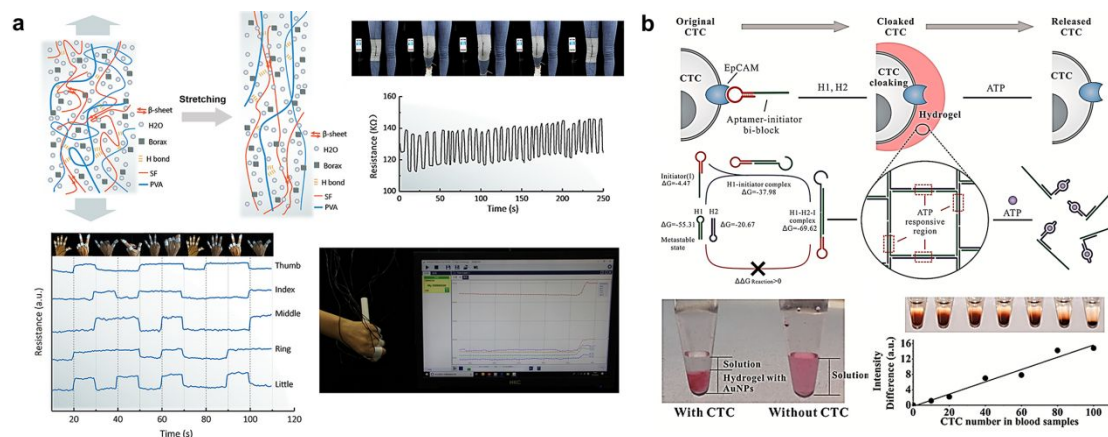


Figure 6. Biomolecule-incorporated hydrogel strain sensors. (a) Protein-based PVA/RSF/borax hydrogel sensor with high stretchability, self-healing, and adhesion properties, which are integrated together and used as a physical sensing platform for human motion detection [Adapted with permission from (⁹⁰), copyright 2019 American Chemical Society]. (b) ATP-aptamer-responsive DNA hydrogel sensor for capturing and releasing of circulating tumor cells with high cell viability. [Adapted with permission from (⁹²), copyright 2019 American Chemical Society].

Different from pure DNA hydrogels, due to a negatively charged nature of DNA, DNA is also used to form a responsive complex through physical interactions with cationic polyelectrolytes or nanocomposites or chemical grafting onto synthetic polymers¹⁴²⁻¹⁴³. Physical DNA-polymer or DNA-composite hydrogels undergo reversible and switchable changes in the morphology, color, and size in response to external stimuli, and thus are often used as smart sensors and devices to monitor binding events. However, physical DNA-polymer hybrid hydrogels usually suffer from weak mechanical strength and poor sensitivity, presumably due to the lack of precise controlling to form ordered structures. Instead of using physical interactions, DNA can be covalently grafted onto or crosslinked with polymers or proteins to construct programmable structures in hydrogel networks. For example, co-assembles with an octapeptides and DNA allowed to fabricate DNA-inspired hydrogel sensors, which can selectively hybridize DNA and generate a fluorescence, with a detection limit of 22 pM. DNA-poly(phenylenevinylene) hybrid hydrogels (DNA/SP-PPV) have been developed for monitoring drug release driven by media pH¹⁴⁴. An ATP-responsive DNA hydrogel can achieve a controllable capture and release of cells by incorporating an ATP aptamer in the clamped HCR (aptamer-triggered clamped HCR, atcHCR) (Figure 6b)⁹². Overall, the unique properties of DNA-based hydrogels are particularly useful for biomolecule detection under biologically-relevant conditions, minimize unwanted probe-probe interactions, and have the potential to hugely increase the analyte storage capacity of these devices. In addition, unlike traditional reversible crosslinks such as DHEBA, the DNA-crosslinks do not require the addition of an

initiator-catalyst system to re-establish dissociated crosslinks.

3. Applications of hydrogel-based sensors

3.1. Hydrogel strain sensors as electronic skins

Human skin as naturally evolved product combines multiple sensations and excellent mechanical properties, which offer a perfect example for developing biomimic devices with stimuli-responsive properties for human-machine interactions. “Hydrogel electronic skins” are considered as artificially intelligent skins, which marry the mutual advantages of hydrogels (e.g. high-water content, soft, biocompatibility, and high stretchability/toughness) and electronic devices (e.g. high electrical conductivity and stimuli-responsiveness)^{15, 145-146}. A transparent LiCl-polyAAm hydrogel sensor was designed as the electronic skins, which can sense 0~1 kPa of pressure change and subtle human movements up to more than 1000 times⁸⁴. Following the similar design strategy, bioinspired mineral ACC/polyAAc/alginate hydrogel electronic skins were developed to sense a gentle human motion (e.g. finger touch, speaking and laughing) with very high pressure sensitivity up to 1 kPa⁶⁵. Zwitterionic poly(MMA-*co*-DMAPS) hydrogels strain sensors by integrating a parallel-plate capacitor with an ionic resistor enabled to mimic mechanoreceptor (detection for 10000 strain change) and thermo-receptor in human skin (10~80 °C) due to temperature-sensitive transition between LCST and UCST.⁶⁶ However, challenges still remain—most of hydrogel-based electronic skins still possess relatively unitary functions. To end this, a more precise and multifunctional electronic skins—LiCl-PVA hydrogel strain sensors (>2000% of biaxial strain) combining with a flexible unit bearing power supply, control, readout and communication units, a stretchable transducer batch, and printed circuit board was successfully constructed as an intelligence electronic skins.¹⁴⁷ This LiCl-PVA hydrogel electronic skin can real-time monitor and control the human body temperature, collect some health information (e.g. blood pressure, heart beating), and trigger drug releases for treatment whenever abnormal physiological signals were received. This electronic skin outperforms most of current hydrogel electronic skin, which is worthy of further exploration of potential bioelectronic applications.

3.2. Hydrogel strain sensors as wrist pulse or cardiac rhythm monitors

Artery pulse in (pre)clinical practice is a significant indicator of arterial blood pressure, cardiac rhythm, and aged blood vessel, which often provides useful information for real-time, non-invasive diagnosis of possible cardiovascular diseases¹⁴⁸⁻¹⁴⁹. Due to the highly flexible and soft matrix of hydrogel strain sensors, hydrogel sensors enable to closely fit the curvature and surface of human skins with underneath of blood vessels, so as to precisely detect three symbolic pulse waves as induced by wrist pulse, blood-pressure, and cardiac rhythm: percussion wave (P or P₁ wave), tidal wave (T or P₂ wave), and diastolic wave (D or P₃ wave), where P₁/P₂ waves are early/late systolic peak pressure and P₃ wave is the diastolic pulse waveform¹⁵⁰⁻¹⁵¹. More interestingly, P₁-wave/P₂-wave (radial artery augmentation index) and the time delay between these two-wave peaks largely reflect the arterial stiffness level, which is highly related to the health condition of people¹⁵². For instance, a number of hydrogel-based wrist pulse/blood-pressure sensors made of PANI-poly(AAm-*co*-HEMA)³⁹, F-polyNIPAM/PANI⁶⁴, AgNWs-polyAAm-PVP⁷², SA/TA/polyAAm⁷⁹, Cu²⁺/polyAAm⁸¹, LiCl-PVA⁸⁵, NaCl-SA/polyAAm⁸⁶, PANI/PSS⁶³, polySBMA/PVA¹²³, Ca²⁺-SA-polyAAc¹⁵³, Agar/NaCl/polyAAm¹⁵⁴, Chitosan-PPy-polyAAc¹⁵⁵, and SA-CNC/polyAAc¹⁵⁶ possessed high sensitivity with a gauge factor of 0.5~3, allowing for tracking irregular pulses, waves, and intervals within 0.1 s. However, the shape,

frequency, and amplitude of pulse signals collected by these hydrogel sensors were still somehow rough, and in some cases, they cannot accurately distinguish percussion (P_1), diastolic (P_2) and tidal (P_3) waves, limiting their further practical applications.

To overcome this detection sensitivity issue, the incorporation of nanoparticles into hydrogels, i.e. PDA-CNTs-poly(AAm-AAc)⁷⁴, MXene-PVA⁷⁵, FSWCNT-PDA-PVA⁷⁷, PDA-PPy-polyAAm¹⁰⁵, CNTs-Egg white¹⁵⁷, SWCNT/polyAAm¹⁵⁸, allows to increase a gauge factor to 3~80 so as to distinguish different pulse waves under 10 kPa. Meanwhile, these wrist pulse/blood-pressure hydrogel sensors enabled to transmit wireless signals to smart phones. Besides hydrogel detection sensitivity (gauge factor), specific contacting area between hydrogel sensors and human body is also important for wrist pulse or blood-pressure. An wireless pressure-sensing device incorporating Ca^{2+} -SA¹⁵⁹ hydrogel microspheres can continuously detect and distinguish characteristic pulse waves from human skin (~25 Pa), consistent with the clinically used wrist pulse detectors. On the other hand, hydrogel strain sensors are still inferior to metal/organic-based (e.g. ZnO-, Pt-, CNT-, Au nanowires-based) pulse sensors in terms of both detection sensitivity and specificity, presumably due to the irreversible fatigue and damage of network structure in hydrogels. Thus, some reversible bonds or self-healable materials should be introduced in such hydrogel sensors.

3.3. Hydrogel strain sensors as visual sensors

Stimuli-responsive hydrogels (e.g. thermal-responsive, glucose-responsive, pH-responsive, and cocaine-responsive hydrogels) possess a general ability to induce volume/size changes (i.e. shrinking or swelling) upon external stimuli. Particularly, when incorporating photonic crystals (PCs) or nanoparticles (PNs) into hydrogel network, it would alter the periodicity layout of PCs and PNs to trigger the transformation of bio-/physical-signals into colorimetric signals, eventually achieving optical changes.¹⁶⁰ A colorful poly(St-MMA-AAm) hydrogel sensor embedded PCs were successfully designed to realize reversible color change from transparent to violet, blue, cyan, green and red in response to different humidity conditions, and the color change almost covered a whole visible range¹⁶¹. Such real-time, optical visual change was determined by expanding or contracting the crosslinked networks upon the increase or decrease of external humidity. Similarly, when incorporating PCs into Si structure, poly(HEMA-co-MMA)-PCs hydrogel sensors can achieve color changes in response to temperature (25 °C~50°C) due to swelling/shrinking-induced viscoelastic deformation. A hybrid protein kinase A (PKA)/PCs hydrogel sensor enables color changes for the label-free detection of kinase (PKA) as evidenced by a redshift, with a lowest detection limit of 2 U/ μ L for 2 h).¹⁶² Moreover, the modified AuNPs with plasmonic nanostructures can also be incorporated into hydrogel sensor as real-time colorimetric visual detectors. A smart colorimetric stretchable plasmonic AuNPs-polyNIPAM hydrogels biosensor was able to achieve rapid, reversible, color changes between red and grayish violet in response to a temperature change from 25 °C~40 °C within 1 s⁶⁸. In general, PCs/AuNPs-incorporated hydrogel sensors hold great promise for wearable healthcare, due to their visual signals by naked eyes, without the needs for any additional detection instruments. However, when applying these visual sensors to wearable healthcare devices, epidermal contortion or human activity often inevitably causes irreversible damage of hydrogel networks and structures, which in turn compromise the performance of these hydrogel sensors. To overcome this issue, we propose to introduce some pattern structures to minimize the stretching of PCs so as to protect their colorimetric response.

3.4 Hydrogel strain sensors as human motions

Like other strain sensors, hydrogel strain sensors enable to capture or distinguish different human motion activities. Current commercial or representative organic/inorganic-based strain sensors made of a combination of CNT, GO, and other conductive materials with elastomeric substrates usually have limited stretchability up to 200%, while hydrogel strain sensors tend to adopt more complex and considerable deformation detection with their higher stretchability (300%~10000%)¹⁶³⁻¹⁶⁴. Multi-scale strains of human motions include large-scale motions (e.g., bending and twisting of hands, arms, and legs with a minimal strain >200%) and small-scale motions (e.g., subtle movements of face, chest, and neck during emotional expression, breathing, and speaking with a minor strain of <50%). Both single-network hydrogel strain sensors (e.g. Cu²⁺-polyAAm⁸¹, MXene-PVA⁷⁵) and double-network hydrogel sensors (e.g. KCl-κ-carrageenan/polyAAm⁸⁰, NaCl-SA/polyAAm⁸⁶, NaCl/SDS-RSF/HPPAAm⁸⁷, SA/TA/polyAAm⁷⁹) were able to detect these human motions. However, it is generally difficult for hydrogel networks to recover to the initial state immediately after undergoing large deformation, thus re-calibration of signal baseline of many hydrogel sensors after several-round tests is required. Therefore, ultra-stretchable hydrogel sensor with good mechanical self-recovery is expected to improve the substantial detection ability for human motion. For instance, when incorporation of PVP-capped AgNWs into polyAAm hydrogel, the resultant hydrogel sensor exhibited extremely high stretchability (>22000%), autonomous self-healing, mechanical compliance, and ultrawide linear response range from a gauge factor of 0.15 at 0-430% of tensile strain to 0.71 at 430-18100% of tensile strain.⁷² Another typical MXene-PVA hydrogel sensor with 3400% of stretchability and good self-recovery were designed to track facial expressions, hand gestures, finger bending, hand writing, and vocal motions. Due to its soft and sticky characteristics, MXene-PVA sensor can readily adhere onto various positions of human skins to a stable and repeatable detection.⁷⁵ Such sensor with great self-recovery can real-time and in situ track large body deformations, spatial gesture movements, and physiological signals for motion behaviors, as well as provide some health evaluation without any calibration, because the quick recovery of cross-linked network would maintain the relatively stable signal baseline.

4. Conclusion and Perspectives

This review provides an update on the current status and developments in hydrogel strain sensors, including their design strategies, preparation methods, functional properties, mechanical sensing mechanisms, and practical applications. Despite great advancements, functional hydrogel strain sensors with excellent electrical, magnetic, optical, and biocompatibility properties are still in their infancy. Current research to date still mainly focuses on the exploration of new stimuli-responsive hydrogel systems, but some fundamental issues need to be addressed.

Conventional hydrogels used for strain sensors usually possess limited mechanical strength and are prone to permanent breakage. Such intrinsic mechanical weakness often renders hydrogel sensors vulnerable to damage under continuous and responsive actions, resulting in the unstable sensitivity and specificity of hydrogel sensors. Lack of dynamic cues and mechanical strength within the hydrogels limit their sensing ability. To remedy this issue, on one hand, introducing self-healing properties to hydrogel sensors would repair structural damage, increase reusability and stability, and restore sensing ability to some extents. On the other hand, use of tough hydrogels (e.g. double-network hydrogels and nanocomposite hydrogels) as a structural platform

to integrate different sensing components is considered as alternative design strategy to enhance their sensing capacity of hydrogel sensors. However, it still remains a great challenge to design and construct self-healing hydrogel sensors, which combines several properties of rapid autonomous self-healing ability, high-mechanical healing efficiency, and easily distinguishable response signals. Also, retaining long-time self-healing of hydrogel sensors is another critical concern particularly under harsh conditions (e.g. underwater, freezing temperature, or salt/acidic solution). When applying hydrogel strain sensors to wearable devices, apart from ultra-stretchability and high mechanical strength, additional robust adhesion to various solid surfaces (e.g. metal, glass, ceramic, wood) and soft materials (e.g. rubber, skin, tissue, organ) are required to maintain high strain sensitivity and stability to detect large human motions and tiny physiological signals. Another research direction is to apply hydrogel sensors for bio-applications, in this regard, hydrogels themselves must be also nontoxic and biocompatible for hydrogel-based skin sensor, blood-pressure sensors, and implanted/injectable sensors. From an experimental viewpoint, it is always unstoppable motivation for materials researchers to explore cutting-edge chemistries and fabrication technologies for designing and synthesizing novel hydrogels with desired properties towards specific sensing applications. In addition, beyond hydrogels, it is also interesting to develop and study organic gels prepared in or containing non-water solvents of varied polarities so as to understand the solvent effect on different aspects of organic gels, to reveal the differences and similarities in gelation process, mechanical properties, toughening mechanisms, and network structures between hydrogels and organic gels, and to expand completely different gel systems for different applications.

In parallel, future efforts should be made to use computational modeling and machine learning technologies, along with polymer chemistry, synthesis, and gelation, to better understand the component-structure-performance relationship of hydrogel materials and to improve the structural-based design of hydrogel sensors and their interactions with target components or exogenous stimuli. Multi-scale simulations should study the deformation and recovery of hydrogels at the atomic, molecular, and macroscopic levels to clarify these issues. Very little work has been done on this front.

Acknowledgement. This review is particularly to thank all current and former collaborators who have been working on different aspects of smart hydrogel materials over years at the Zheng lab. We also thank Louisa Wang from Hathaway Brown School for her hard work in our lab during summer.

References

1. Drury, J. L.; Mooney, D. J., Hydrogels for tissue engineering: scaffold design variables and applications. *Biomaterials* **2003**, *24* (24), 4337-4351.
2. Ma, P. X., Scaffolds for tissue fabrication. *Materials Today* **2004**, *7* (5), 30-40.
3. Sayyar, S.; Murray, E.; Thompson, B. C.; Chung, J.; Officer, D. L.; Gambhir, S.; Spinks, G. M.; Wallace, G. G., Processable conducting graphene/chitosan hydrogels for tissue engineering. *Journal of Materials Chemistry B* **2015**, *3* (3), 481-490.
4. Matthew B. Applegate; Jeannine Coburn; Benjamin P. Partlow; Jodie E. Moreau; Jessica P. Mondia; Benedetto Marelli; David L. Kaplan; Omenetto, F. G., Laser-based three-dimensional multiscale micropatterning of biocompatible hydrogels for customized tissue engineering scaffolds. *Proc Natl Acad Sci U S A* **2015**, *112* (39), 12052-12057.
5. Kim, Y.-M.; Kim, C.-H.; Song, S.-C., Injectable Ternary Nanocomplex Hydrogel for Long-Term Chemical Drug/Gene Dual Delivery. *ACS Macro Letters* **2016**, *5* (3), 297-300.
6. Arti Vashist; Atul Vashist; Y. K. Gupta; Ahmad, S., Recent advances in hydrogel based drug delivery systems for the human body. *J. Mater. Chem. B* **2014**, *2* (2), 147-166.
7. Feng, Q.; Xu, J.; Zhang, K.; Yao, H.; Zheng, N.; Zheng, L.; Wang, J.; Wei, K.; Xiao, X.; Qin, L.; Bian, L., Dynamic and Cell-Infiltratable Hydrogels as Injectable Carrier of Therapeutic Cells and Drugs for Treating Challenging Bone Defects. *ACS Cent Sci* **2019**, *5* (3), 440-450.
8. He, H.; Xiao, Z.; Zhou, Y.; Chen, A.; Xuan, X.; Li, Y.; Guo, X.; Zheng, J.; Xiao, J.; Wu, J., Zwitterionic poly(sulfobetaine methacrylate) hydrogels with optimal mechanical properties for improving wound healing in vivo. *Journal of Materials Chemistry B* **2019**, *7* (10), 1697-1707.
9. di Luca, M.; Curcio, M.; Valli, E.; Cirillo, G.; Voli, F.; Butini, M. E.; Farfalla, A.; Pantuso, E.; Leggio, A.; Nicoletta, F. P.; Tavanti, A.; Iemma, F.; Vittorio, O., Combining antioxidant hydrogels with self-assembled microparticles for multifunctional wound dressings. *Journal of Materials Chemistry B* **2019**, *7* (27), 4361-4370.
10. Li, S.; Dong, S.; Xu, W.; Tu, S.; Yan, L.; Zhao, C.; Ding, J.; Chen, X., Antibacterial Hydrogels. *Adv Sci (Weinh)* **2018**, *5* (5), 1700527.
11. Han, L.; Yan, L.; Wang, K.; Fang, L.; Zhang, H.; Tang, Y.; Ding, Y.; Weng, L.-T.; Xu, J.; Weng, J.; Liu, Y.; Ren, F.; Lu, X., Tough, self-healable and tissue-adhesive hydrogel with tunable multifunctionality. *NPG Asia Materials* **2017**, *9* (4), e372-e372.
12. Schroeder, T. B. H.; Guha, A.; Lamoureux, A.; VanRenterghem, G.; Sept, D.; Shtein, M.; Yang, J.; Mayer, M., An electric-eel-inspired soft power source from stacked hydrogels. *Nature* **2017**, *552* (7684), 214-218.
13. Kim, J.; Kim, M.; Lee, M. S.; Kim, K.; Ji, S.; Kim, Y. T.; Park, J.; Na, K.; Bae, K. H.; Kyun Kim, H.; Bien, F.; Young Lee, C.; Park, J. U., Wearable smart sensor systems integrated on soft contact lenses for wireless ocular diagnostics. *Nat Commun* **2017**, *8*, 14997.
14. Huang, J. F.; Zhong, J.; Chen, G. P.; Lin, Z. T.; Deng, Y.; Liu, Y. L.; Cao, P. Y.; Wang, B.; Wei, Y.; Wu, T.; Yuan, J.; Jiang, G. B., A Hydrogel-Based Hybrid Theranostic Contact Lens for Fungal Keratitis. *ACS Nano* **2016**, *10* (7), 6464-73.
15. Yang, C.; Suo, Z., Hydrogel ionotronics. *Nature Reviews Materials* **2018**, *3* (6), 125-142.

16. Li, H.; Lv, T.; Sun, H.; Qian, G.; Li, N.; Yao, Y.; Chen, T., Ultrastretchable and superior healable supercapacitors based on a double cross-linked hydrogel electrolyte. *Nat Commun* **2019**, *10* (1), 536.
17. Imani, S.; Bandodkar, A. J.; Mohan, A. M.; Kumar, R.; Yu, S.; Wang, J.; Mercier, P. P., A wearable chemical-electrophysiological hybrid biosensing system for real-time health and fitness monitoring. *Nat Commun* **2016**, *7*, 11650.
18. Cao, Y.; Tan, Y. J.; Li, S.; Lee, W. W.; Guo, H.; Cai, Y.; Wang, C.; Tee, B. C. K., Self-healing electronic skins for aquatic environments. *Nature Electronics* **2019**, *2* (2), 75-82.
19. Yu, Y.; Yuk, H.; Parada, G. A.; Wu, Y.; Liu, X.; Nabzdyk, C. S.; Youcef-Toumi, K.; Zang, J.; Zhao, X., Multifunctional "Hydrogel Skins" on Diverse Polymers with Arbitrary Shapes. *Adv Mater* **2019**, *31* (7), e1807101.
20. Zhao, Z.; Wang, C.; Yan, H.; Liu, Y., Soft Robotics Programmed with Double Crosslinking DNA Hydrogels. *Advanced Functional Materials* **2019**, *29* (45), 1905911.
21. Cianchetti, M.; Laschi, C.; Menciassi, A.; Dario, P., Biomedical applications of soft robotics. *Nature Reviews Materials* **2018**, *3* (6), 143-153.
22. Sitti, M., Miniature soft robots — road to the clinic. *Nature Reviews Materials* **2018**, *3* (6), 74-75.
23. Ge, G.; Zhang, Y.; Shao, J.; Wang, W.; Si, W.; Huang, W.; Dong, X., Stretchable, Transparent, and Self-Patterned Hydrogel-Based Pressure Sensor for Human Motions Detection. *Advanced Functional Materials* **2018**, *28* (32), 1802576.
24. Shuai Xu; Arun Jayaraman; Rogers, J. A., Skin sensors are the future of health care. *Nature* **2019**, *571*, 319-321.
25. Liu, X.; Steiger, C.; Lin, S.; Parada, G. A.; Liu, J.; Chan, H. F.; Yuk, H.; Phan, N. V.; Collins, J.; Tamang, S.; Traverso, G.; Zhao, X., Ingestible hydrogel device. *Nat Commun* **2019**, *10* (1), 493.
26. Gao, Y.; Song, J.; Li, S.; Elowsky, C.; Zhou, Y.; Ducharme, S.; Chen, Y. M.; Zhou, Q.; Tan, L., Hydrogel microphones for stealthy underwater listening. *Nat Commun* **2016**, *7*, 12316.
27. Hyunjae Lee; Changyeong Song; Yong Seok Hong; Min Sung Kim; Hye Rim Cho; Taegy Kang; Kwangsoo Shin; Seung Hong Choi; Taeghwan Hyeon; Kim, D.-H., Wearable/disposable sweat-based glucose monitoring device with multistage transdermal drug delivery module. *Science Advances* **2017**, *3* (3), e1601314.
28. Xiong Pu; Mengmeng Liu; Xiangyu Chen; Jiangman Sun; Chunhua Du; Yang Zhang; Junyi Zhai; Weiguo Hu; Wang, Z. L., Ultrastretchable, transparent triboelectric nanogenerator as electronic skin for biomechanical energy harvesting and tactile sensing. *3* **2017**, *5* (e1700015).
29. Li, P.; Zhang, D.; Zhang, Y.; Lu, W.; Wang, W.; Chen, T., Ultrafast and Efficient Detection of Formaldehyde in Aqueous Solutions Using Chitosan-based Fluorescent Polymers. *ACS Sens* **2018**, *3* (11), 2394-2401.
30. Zhang, D.; Fu, Y.; Huang, L.; Zhang, Y.; Ren, B.; Zhong, M.; Yang, J.; Zheng, J., Integration of antifouling and antibacterial properties in salt-responsive hydrogels with surface regeneration capacity. *Journal of Materials Chemistry B* **2018**, *6* (6), 950-960.
31. Lu, W.; Ma, C.; Zhang, D.; Le, X.; Zhang, J.; Huang, Y.; Huang, C.-F.; Chen, T., Real-Time in Situ Investigation of Supramolecular Shape Memory Process by Fluorescence Switching. *The Journal of Physical Chemistry C* **2018**, *122* (17), 9499-9506.
32. Konieczynska, M. D.; Villacamacho, J. C.; Ghobril, C.; Perezviloria, M.; Tevis, K. M.; Blessing, W. A.; Nazarian, A.; Rodriguez, E. K.; Grinstaff, M. W., On-Demand

- Dissolution of a Dendritic Hydrogel-based Dressing for Second-Degree Burn Wounds through Thiol-Thioester Exchange Reaction. *Angewandte Chemie* **2016**, *55* (34), 9984-9987.
33. Roy, N.; Saha, N.; Kitano, T.; Saha, P., Development and Characterization of Novel Medicated Hydrogels for Wound Dressing. *Soft Materials* **2010**, *8* (2), 130-148.
34. Mirani, B.; Pagan, E.; Currie, B.; Siddiqui, M. A.; Hosseinzadeh, R.; Mostafalu, P.; Zhang, Y. S.; Ghahary, A.; Akbari, M., An Advanced Multifunctional Hydrogel-Based Dressing for Wound Monitoring and Drug Delivery. *Advanced Healthcare Materials* **2017**, *6* (19), 1700718.
35. Sakai, S.; Tsumura, M.; Inoue, M.; Koga, Y.; Fukano, K.; Taya, M., Polyvinyl alcohol-based hydrogel dressing gellable on-wound via a co-enzymatic reaction triggered by glucose in the wound exudate. *Journal of Materials Chemistry B* **2013**, *1* (38), 5067-5075.
36. Zhang, D.; Zhang, Y.; Lu, W.; Le, X.; Li, P.; Huang, L.; Zhang, J.; Yang, J.; Serpe, M. J.; Chen, D.; Chen, T., Fluorescent Hydrogel-Coated Paper/Textile as Flexible Chemosensor for Visual and Wearable Mercury(II) Detection. *Advanced Materials Technologies* **2019**, *4* (1), 1800201.
37. Stashak, T. S.; Farstvedt, E.; Othic, A., Update on wound dressings: Indications and best use. *Clinical Techniques in Equine Practice* **2004**, *3* (2), 148-163.
38. Yetisen, A. K.; Butt, H.; da Cruz Vasconcellos, F.; Montelongo, Y.; Davidson, C. A. B.; Blyth, J.; Chan, L.; Carmody, J. B.; Vignolini, S.; Steiner, U.; Baumberg, J. J.; Wilkinson, T. D.; Lowe, C. R., Light-Directed Writing of Chemically Tunable Narrow-Band Holographic Sensors. *Advanced Optical Materials* **2014**, *2* (3), 250-254.
39. Wang, Z.; Chen, J.; Cong, Y.; Zhang, H.; Xu, T.; Nie, L.; Fu, J., Ultrastretchable Strain Sensors and Arrays with High Sensitivity and Linearity Based on Super Tough Conductive Hydrogels. *Chemistry of Materials* **2018**, *30* (21), 8062-8069.
40. Chen, H.; Yang, F.; Chen, Q.; Zheng, J., A Novel Design of Multi-Mechanoresponsive and Mechanically Strong Hydrogels. *Adv Mater* **2017**, *29* (21).
41. Zhang, Y.; Ren, B.; Yang, F.; Cai, Y.; Chen, H.; Wang, T.; Feng, Z.; Tang, J.; Xu, J.; Zheng, J., Micellar-incorporated hydrogels with highly tough, mechanoresponsive, and self-recovery properties for strain-induced color sensors. *Journal of Materials Chemistry C* **2018**, *6* (43), 11536-11551.
42. Xiao, S.; Yang, Y.; Zhong, M.; Chen, H.; Zhang, Y.; Yang, J.; Zheng, J., Salt-Responsive Bilayer Hydrogels with Pseudo-Double-Network Structure Actuated by Polyelectrolyte and Antipolyelectrolyte Effects. *ACS Appl Mater Interfaces* **2017**, *9* (24), 20843-20851.
43. Xiao, S.; Zhang, M.; He, X.; Huang, L.; Zhang, Y.; Ren, B.; Zhong, M.; Chang, Y.; Yang, J.; Zheng, J., Dual Salt- and Thermoresponsive Programmable Bilayer Hydrogel Actuators with Pseudo-Interpenetrating Double-Network Structures. *ACS Appl Mater Interfaces* **2018**, *10* (25), 21642-21653.
44. Naydenova, I.; Jallapuram, R.; Toal, V.; Martin, S., A visual indication of environmental humidity using a color changing hologram recorded in a self-developing photopolymer. *Applied Physics Letters* **2008**, *92* (3), 031109.
45. Ma, C.; Li, T.; Zhao, Q.; Yang, X.; Wu, J.; Luo, Y.; Xie, T., Supramolecular Lego assembly towards three-dimensional multi-responsive hydrogels. *Adv Mater* **2014**, *26* (32), 5665-9.
46. Wei, S.; Lu, W.; Le, X.; Ma, C.; Lin, H.; Wu, B.; Zhang, J.; Theato, P.; Chen, T., Bioinspired Synergistic Fluorescence-Color-Switchable Polymeric Hydrogel Actuators. *Angew Chem Int Ed Engl* **2019**, *58* (45), 16243-16251.

47. Zheng, J.; Xiao, P.; Le, X.; Lu, W.; Théato, P.; Ma, C.; Du, B.; Zhang, J.; Huang, Y.; Chen, T., Mimosa inspired bilayer hydrogel actuator functioning in multi-environments. *Journal of Materials Chemistry C* **2018**, *6* (6), 1320-1327.
48. Wang, J.; Wang, J.; Chen, Z.; Fang, S.; Zhu, Y.; Baughman, R. H.; Jiang, L., Tunable, Fast, Robust Hydrogel Actuators Based on Evaporation-Programmed Heterogeneous Structures. *Chemistry of Materials* **2017**, *29* (22), 9793-9801.
49. Wang, H.; Ji, X.; Li, Z.; Huang, F., Fluorescent Supramolecular Polymeric Materials. *Adv Mater* **2017**, *29* (14).
50. Voorhaar, L.; Hoogenboom, R., Supramolecular polymer networks: hydrogels and bulk materials. *Chem Soc Rev* **2016**, *45* (14), 4013-31.
51. Ding, X.; Wang, Y., Weak Bond-Based Injectable and Stimuli Responsive Hydrogels for Biomedical Applications. *J Mater Chem B* **2017**, *5* (5), 887-906.
52. Moser, R.; Kettlgruber, G.; Siket, C. M.; Drack, M.; Graz, I. M.; Cakmak, U.; Major, Z.; Kaltenbrunner, M.; Bauer, S., From Playroom to Lab: Tough Stretchable Electronics Analyzed with a Tabletop Tensile Tester Made from Toy-Bricks. *Adv Sci (Weinh)* **2016**, *3* (4), 1500396.
53. Zhao, X.; Chen, F.; Li, Y.; Lu, H.; Zhang, N.; Ma, M., Bioinspired ultra-stretchable and anti-freezing conductive hydrogel fibers with ordered and reversible polymer chain alignment. *Nat Commun* **2018**, *9* (1), 3579.
54. Zhang, J.; Feng, W.; Zhang, H.; Wang, Z.; Calcaterra, H. A.; Yeom, B.; Hu, P. A.; Kotov, N. A., Multiscale deformations lead to high toughness and circularly polarized emission in helical nacre-like fibres. *Nat Commun* **2016**, *7*, 10701.
55. Chortos, A.; Liu, J.; Bao, Z., Pursuing prosthetic electronic skin. *Nat Mater* **2016**, *15* (9), 937-50.
56. Shao, Y.; Jia, H.; Cao, T.; Liu, D., Supramolecular Hydrogels Based on DNA Self-Assembly. *Acc Chem Res* **2017**, *50* (4), 659-668.
57. Frederix, P. W.; Scott, G. G.; Abul-Haija, Y. M.; Kalafatovic, D.; Pappas, C. G.; Javid, N.; Hunt, N. T.; Ulijn, R. V.; Tuttle, T., Exploring the sequence space for (tri-)peptide self-assembly to design and discover new hydrogels. *Nat Chem* **2015**, *7* (1), 30-7.
58. Lu, W.; Huang, C.; Hong, K.; Kang, N.-G.; Mays, J. W., Poly(1-adamantyl acrylate): Living Anionic Polymerization, Block Copolymerization, and Thermal Properties. *Macromolecules* **2016**, *49* (24), 9406-9414.
59. Luo, F.; Sun, T. L.; Nakajima, T.; Kurokawa, T.; Zhao, Y.; Sato, K.; Ihsan, A. B.; Li, X.; Guo, H.; Gong, J. P., Oppositely charged polyelectrolytes form tough, self-healing, and rebuildable hydrogels. *Adv Mater* **2015**, *27* (17), 2722-7.
60. Yue, K.; Trujillo-de Santiago, G.; Alvarez, M. M.; Tamayol, A.; Annabi, N.; Khademhosseini, A., Synthesis, properties, and biomedical applications of gelatin methacryloyl (GelMA) hydrogels. *Biomaterials* **2015**, *73*, 254-71.
61. Xing, J. F.; Zheng, M. L.; Duan, X. M., Two-photon polymerization microfabrication of hydrogels: an advanced 3D printing technology for tissue engineering and drug delivery. *Chem Soc Rev* **2015**, *44* (15), 5031-9.
62. Tien, H. P.; Hoa, P.; Toan, N. C.; Dat, N. T.; Ryeol, C. H., A Highly Flexible, Stretchable and Ultra-thin Piezoresistive Tactile Sensor Array using PAM/PEDOT:PSS Hydrogel. *2017 14th International Conference on Ubiquitous Robots and Ambient Intelligence (URAI)* **2017**, 950-955.
63. Chen, J.; Peng, Q.; Thundat, T.; Zeng, H., Stretchable, Injectable, and Self-Healing Conductive Hydrogel Enabled by Multiple Hydrogen Bonding toward Wearable Electronics. *Chemistry of Materials* **2019**, *31* (12), 4553-4563.

64. Wang, Z.; Zhou, H.; Chen, W.; Li, Q.; Yan, B.; Jin, X.; Ma, A.; Liu, H.; Zhao, W., Dually Synergetic Network Hydrogels with Integrated Mechanical Stretchability, Thermal Responsiveness, and Electrical Conductivity for Strain Sensors and Temperature Alertors. *ACS Appl Mater Interfaces* **2018**, *10* (16), 14045-14054.
65. Lei, Z.; Wang, Q.; Sun, S.; Zhu, W.; Wu, P., A Bioinspired Mineral Hydrogel as a Self-Healable, Mechanically Adaptable Ionic Skin for Highly Sensitive Pressure Sensing. *Adv Mater* **2017**, *29* (22).
66. Lei, Z.; Wu, P., Zwitterionic Skins with a Wide Scope of Customizable Functionalities. *ACS Nano* **2018**, *12* (12), 12860-12868.
67. Luo, X. L.; Xu, J. J.; Zhang, Q.; Yang, G. J.; Chen, H. Y., Electrochemically deposited chitosan hydrogel for horseradish peroxidase immobilization through gold nanoparticles self-assembly. *Biosens Bioelectron* **2005**, *21* (1), 190-6.
68. Choe, A.; Yeom, J.; Shanker, R.; Kim, M. P.; Kang, S.; Ko, H., Stretchable and wearable colorimetric patches based on thermoresponsive plasmonic microgels embedded in a hydrogel film. *NPG Asia Materials* **2018**, *10* (9), 912-922.
69. Song, S. H.; Park, J. H.; Chitnis, G.; Siegel, R. A.; Ziaie, B., A wireless chemical sensor featuring iron oxide nanoparticle-embedded hydrogels. *Sensors and Actuators B: Chemical* **2014**, *193*, 925-930.
70. Li, L.; Pan, L.; Ma, Z.; Yan, K.; Cheng, W.; Shi, Y.; Yu, G., All Inkjet-Printed Amperometric Multiplexed Biosensors Based on Nanostructured Conductive Hydrogel Electrodes. *Nano Lett* **2018**, *18* (6), 3322-3327.
71. Dongyuan Zhai; Borui Liu; Yi Shi; Lijia Pan; Yaqun Wang; Wenbo Li; Rong Zhang; Yu, G., Highly Sensitive Glucose Sensor Based on Pt Nanoparticle/Polyaniline Hydrogel Heterostructures. *ACS Nano* **2013**, *7*, 3540-3546.
72. Zhang, H.; Niu, W.; Zhang, S., Extremely Stretchable and Self-Healable Electrical Skin with Mechanical Adaptability, an Ultrawide Linear Response Range, and Excellent Temperature Tolerance. *ACS Appl Mater Interfaces* **2019**, *11* (27), 24639-24647.
73. Gu, H.; Zhang, H.; Ma, C.; Sun, H.; Liu, C.; Dai, K.; Zhang, J.; Wei, R.; Ding, T.; Guo, Z., Smart strain sensing organic-inorganic hybrid hydrogels with nano barium ferrite as the cross-linker. *Journal of Materials Chemistry C* **2019**, *7* (8), 2353-2360.
74. Han, L.; Liu, K.; Wang, M.; Wang, K.; Fang, L.; Chen, H.; Zhou, J.; Lu, X., Mussel-Inspired Adhesive and Conductive Hydrogel with Long-Lasting Moisture and Extreme Temperature Tolerance. *Advanced Functional Materials* **2018**, *28* (3), 1704195.
75. Yi-Zhou Zhang; Kang Hyuck Lee; Dalaver H. Anjum; Rachid Sougrat; Qiu Jiang; Hyunho Kim; Alshareef, H. N., MXenes stretch hydrogel sensor performance to new limits. *Science Advances* **2018**, *4* (eaat0098).
76. Pan, X.; Wang, Q.; He, P.; Liu, K.; Ni, Y.; Chen, L.; Ouyang, X.; Huang, L.; Wang, H.; Xu, S., A bionic tactile plastic hydrogel-based electronic skin constructed by a nerve-like nanonetwork combining stretchable, compliant, and self-healing properties. *Chemical Engineering Journal* **2020**, *379*, 122271.
77. Liao, M.; Wan, P.; Wen, J.; Gong, M.; Wu, X.; Wang, Y.; Shi, R.; Zhang, L., Wearable, Healable, and Adhesive Epidermal Sensors Assembled from Mussel-Inspired Conductive Hybrid Hydrogel Framework. *Advanced Functional Materials* **2017**, *27* (48), 1703852.
78. Cai, G.; Wang, J.; Qian, K.; Chen, J.; Li, S.; Lee, P. S., Extremely Stretchable Strain Sensors Based on Conductive Self-Healing Dynamic Cross-Links Hydrogels for Human-Motion Detection. *Adv Sci (Weinh)* **2017**, *4* (2), 1600190.

79. Qiao, H.; Qi, P.; Zhang, X.; Wang, L.; Tan, Y.; Luan, Z.; Xia, Y.; Li, Y.; Sui, K., Multiple Weak H-Bonds Lead to Highly Sensitive, Stretchable, Self-Adhesive, and Self-Healing Ionic Sensors. *ACS Appl Mater Interfaces* **2019**, *11* (8), 7755-7763.
80. Liu, S.; Li, L., Ultrastretchable and Self-Healing Double-Network Hydrogel for 3D Printing and Strain Sensor. *ACS Appl Mater Interfaces* **2017**, *9* (31), 26429-26437.
81. Fan, W.; Zhang, X.; Cui, H.; Liu, C.; Li, Y.; Xia, Y.; Sui, K., Direct Current-Powered High-Performance Ionic Hydrogel Strain Sensor Based on Electrochemical Redox Reaction. *ACS Appl Mater Interfaces* **2019**, *11* (27), 24289-24297.
82. Chen, H.; Ren, X.; Gao, G., Skin-Inspired Gels with Toughness, Antifreezing, Conductivity, and Remoldability. *ACS Appl Mater Interfaces* **2019**, *11* (31), 28336-28344.
83. Zhang, Q.; Liu, X.; Duan, L.; Gao, G., Ultra-stretchable wearable strain sensors based on skin-inspired adhesive, tough and conductive hydrogels. *Chemical Engineering Journal* **2019**, *365*, 10-19.
84. Sun, J. Y.; Keplinger, C.; Whitesides, G. M.; Suo, Z., Ionic skin. *Adv Mater* **2014**, *26* (45), 7608-14.
85. Chong-Chan Kim; Hyun-Hee Lee; Kyu Hwan Oh; Sun, J.-Y., Highly stretchable, transparent ionic touch panel. *Science* **2016**, *353*, 682-687.
86. Zhang, X.; Sheng, N.; Wang, L.; Tan, Y.; Liu, C.; Xia, Y.; Nie, Z.; Sui, K., Supramolecular nanofibrillar hydrogels as highly stretchable, elastic and sensitive ionic sensors. *Materials Horizons* **2019**, *6* (2), 326-333.
87. Chen, F.; Lu, S.; Zhu, L.; Tang, Z.; Wang, Q.; Qin, G.; Yang, J.; Sun, G.; Zhang, Q.; Chen, Q., Conductive regenerated silk-fibroin-based hydrogels with integrated high mechanical performances. *Journal of Materials Chemistry B* **2019**, *7* (10), 1708-1715.
88. Cheng, S.; Narang, Y. S.; Yang, C.; Suo, Z.; Howe, R. D., Stick-On Large-Strain Sensors for Soft Robots. *Advanced Materials Interfaces* **2019**, 1900985.
89. Ren, Y.; Guo, J.; Liu, Z.; Sun, Z.; Wu, Y.; Liu, L.; Yan, F., Ionic liquid-based click-ionogels. *Science Advances* **2019**, *5*, 1-10.
90. Yang, N.; Qi, P.; Ren, J.; Yu, H.; Liu, S.; Li, J.; Chen, W.; Kaplan, D. L.; Ling, S., Polyvinyl Alcohol/Silk Fibroin/Borax Hydrogel Ionotronics: A Highly Stretchable, Self-Healable, and Biocompatible Sensing Platform. *ACS Appl Mater Interfaces* **2019**, *11* (26), 23632-23638.
91. Wang, R.; Li, Y., Hydrogel based QCM aptasensor for detection of avian influenza virus. *Biosens Bioelectron* **2013**, *42*, 148-55.
92. Song, P.; Ye, D.; Zuo, X.; Li, J.; Wang, J.; Liu, H.; Hwang, M. T.; Chao, J.; Su, S.; Wang, L.; Shi, J.; Wang, L.; Huang, W.; Lal, R.; Fan, C., DNA Hydrogel with Aptamer-Toehold-Based Recognition, Cloaking, and Decloaking of Circulating Tumor Cells for Live Cell Analysis. *Nano Lett* **2017**, *17* (9), 5193-5198.
93. Buenger, D.; Topuz, F.; Groll, J., Hydrogels in sensing applications. *Progress in Polymer Science* **2012**, *37* (12), 1678-1719.
94. Wu, J.; Wu, Z.; Lu, X.; Han, S.; Yang, B. R.; Gui, X.; Tao, K.; Miao, J.; Liu, C., Ultrastretchable and Stable Strain Sensors Based on Antifreezing and Self-Healing Ionic Organohydrogels for Human Motion Monitoring. *ACS Appl Mater Interfaces* **2019**, *11* (9), 9405-9414.
95. Gan, D.; Huang, Z.; Wang, X.; Jiang, L.; Wang, C.; Zhu, M.; Ren, F.; Fang, L.; Wang, K.; Xie, C.; Lu, X., Graphene Oxide-Templated Conductive and Redox-Active Nanosheets Incorporated Hydrogels for Adhesive Bioelectronics. *Advanced Functional Materials* **2019**, 1907678.

96. Hou, C.; Wang, H.; Zhang, Q.; Li, Y.; Zhu, M., Highly conductive, flexible, and compressible all-graphene passive electronic skin for sensing human touch. *Adv Mater* **2014**, *26* (29), 5018-24.
97. Song, H. S.; Kwon, O. S.; Kim, J. H.; Conde, J.; Artzi, N., 3D hydrogel scaffold doped with 2D graphene materials for biosensors and bioelectronics. *Biosens Bioelectron* **2017**, *89* (Pt 1), 187-200.
98. Wu, J.; Tao, K.; Zhang, J.; Guo, Y.; Miao, J.; Norford, L. K., Chemically functionalized 3D graphene hydrogel for high performance gas sensing. *Journal of Materials Chemistry A* **2016**, *4* (21), 8130-8140.
99. Han, L.; Lu, X.; Wang, M.; Gan, D.; Deng, W.; Wang, K.; Fang, L.; Liu, K.; Chan, C. W.; Tang, Y.; Weng, L. T.; Yuan, H., A Mussel-Inspired Conductive, Self-Adhesive, and Self-Healable Tough Hydrogel as Cell Stimulators and Implantable Bioelectronics. *Small* **2017**, *13* (2).
100. Long, Y.-Z.; Li, M.-M.; Gu, C.; Wan, M.; Duvail, J.-L.; Liu, Z.; Fan, Z., Recent advances in synthesis, physical properties and applications of conducting polymer nanotubes and nanofibers. *Progress in Polymer Science* **2011**, *36* (10), 1415-1442.
101. Lota, G.; Fic, K.; Frackowiak, E., Carbon nanotubes and their composites in electrochemical applications. *Energy & Environmental Science* **2011**, *4* (5), 1592.
102. He, Y.; Gui, Q.; Wang, Y.; Wang, Z.; Liao, S.; Wang, Y., A Polypyrrole Elastomer Based on Confined Polymerization in a Host Polymer Network for Highly Stretchable Temperature and Strain Sensors. *Small* **2018**, *14* (19), e1800394.
103. Chowdhury, A. D.; Takemura, K.; Li, T. C.; Suzuki, T.; Park, E. Y., Electrical pulse-induced electrochemical biosensor for hepatitis E virus detection. *Nat Commun* **2019**, *10* (1), 3737.
104. An, B. W.; Heo, S.; Ji, S.; Bien, F.; Park, J. U., Transparent and flexible fingerprint sensor array with multiplexed detection of tactile pressure and skin temperature. *Nat Commun* **2018**, *9* (1), 2458.
105. Han, L.; Yan, L.; Wang, M.; Wang, K.; Fang, L.; Zhou, J.; Fang, J.; Ren, F.; Lu, X., Transparent, Adhesive, and Conductive Hydrogel for Soft Bioelectronics Based on Light-Transmitting Polydopamine-Doped Polypyrrole Nanofibrils. *Chemistry of Materials* **2018**, *30* (16), 5561-5572.
106. Li, P.; Jin, Z.; Peng, L.; Zhao, F.; Xiao, D.; Jin, Y.; Yu, G., Stretchable All-Gel-State Fiber-Shaped Supercapacitors Enabled by Macromolecularly Interconnected 3D Graphene/Nanostructured Conductive Polymer Hydrogels. *Adv Mater* **2018**, *30* (18), e1800124.
107. Shi, Y.; Ma, C.; Peng, L.; Yu, G., Conductive "Smart" Hybrid Hydrogels with PNIPAM and Nanostructured Conductive Polymers. *Advanced Functional Materials* **2015**, *25* (8), 1219-1225.
108. Bryan, A. M.; Santino, L. M.; Lu, Y.; Acharya, S.; D'Arcy, J. M., Conducting Polymers for Pseudocapacitive Energy Storage. *Chemistry of Materials* **2016**, *28* (17), 5989-5998.
109. Kishi, R.; Kubota, K.; Miura, T.; Yamaguchi, T.; Okuzaki, H.; Osada, Y., Mechanically tough double-network hydrogels with high electronic conductivity. *J. Mater. Chem. C* **2014**, *2* (4), 736-743.
110. Dai, T.; Qing, X.; Lu, Y.; Xia, Y., Conducting hydrogels with enhanced mechanical strength. *Polymer* **2009**, *50* (22), 5236-5241.
111. You, J.; Xie, S.; Cao, J.; Ge, H.; Xu, M.; Zhang, L.; Zhou, J., Quaternized Chitosan/Poly(acrylic acid) Polyelectrolyte Complex Hydrogels with Tough, Self-Recovery, and Tunable Mechanical Properties. *Macromolecules* **2016**, *49* (3), 1049-1059.

112. Huang, Y.; Zhong, M.; Shi, F.; Liu, X.; Tang, Z.; Wang, Y.; Huang, Y.; Hou, H.; Xie, X.; Zhi, C., An Intrinsically Stretchable and Compressible Supercapacitor Containing a Polyacrylamide Hydrogel Electrolyte. *Angew Chem Int Ed Engl* **2017**, *56* (31), 9141-9145.
113. Jia, Z.; Zeng, Y.; Tang, P.; Gan, D.; Xing, W.; Hou, Y.; Wang, K.; Xie, C.; Lu, X., Conductive, Tough, Transparent, and Self-Healing Hydrogels Based on Catechol-Metal Ion Dual Self-Catalysis. *Chemistry of Materials* **2019**, *31* (15), 5625-5632.
114. Thiburce, Q.; Campbell, A. J., Low-Voltage Polyelectrolyte-Gated Polymer Field-Effect Transistors Gravure Printed at High Speed on Flexible Plastic Substrates. *Advanced Electronic Materials* **2017**, *3* (2), 1600421.
115. Ali, S.; Bleuel, M.; Prabhu, V. M., Lower Critical Solution Temperature in Polyelectrolyte Complex Coacervates. *ACS Macro Letters* **2019**, *8* (3), 289-293.
116. Wang, L.; Gao, G.; Zhou, Y.; Xu, T.; Chen, J.; Wang, R.; Zhang, R.; Fu, J., Tough, Adhesive, Self-Healable, and Transparent Ionically Conductive Zwitterionic Nanocomposite Hydrogels as Skin Strain Sensors. *ACS Appl Mater Interfaces* **2019**, *11* (3), 3506-3515.
117. Kim, J.; Nayak, S.; Lyon, L. A., Bioresponsive hydrogel microlenses. *J Am Chem Soc* **2005**, *127* (26), 9588-9592.
118. Lei, Z.; Wu, P., A supramolecular biomimetic skin combining a wide spectrum of mechanical properties and multiple sensory capabilities. *Nat Commun* **2018**, *9* (1), 1134.
119. Lin, S.; Yuan, C.; Ke, A.; Quan, Z., Electrical response characterization of PVA-P(AA/AMPS) IPN hydrogels in aqueous Na₂SO₄ solution. *Sensors and Actuators B: Chemical* **2008**, *134* (1), 281-286.
120. Liu, F.; Urban, M. W., Recent advances and challenges in designing stimuli-responsive polymers. *Progress in Polymer Science* **2010**, *35* (1-2), 3-23.
121. Bouillot, P.; Vincent, B., A comparison of the swelling behaviour of copolymer and interpenetrating network microgel particles. *Colloid and Polymer Science* **2000**, *278* (1), 74-79.
122. Xu, Y.; Ghag, O.; Reimann, M.; Sitterle, P.; Chatterjee, P.; Nofen, E.; Yu, H.; Jiang, H.; Dai, L. L., Development of visible-light responsive and mechanically enhanced "smart" UCST interpenetrating network hydrogels. *Soft Matter* **2017**, *14* (1), 151-160.
123. Wang, Z.; Chen, J.; Wang, L.; Gao, G.; Zhou, Y.; Wang, R.; Xu, T.; Yin, J.; Fu, J., Flexible and wearable strain sensors based on tough and self-adhesive ion conducting hydrogels. *Journal of Materials Chemistry B* **2019**, *7* (1), 24-29.
124. Izawa, H.; Kadokawa, J.-i., Preparation and characterizations of functional ionic liquid-gel and hydrogel materials of xanthan gum. *Journal of Materials Chemistry* **2010**, *20* (25), 5235.
125. Yan, J.; Rodrigues, M.-T. F.; Song, Z.; Li, H.; Xu, H.; Liu, H.; Wu, J.; Xu, Y.; Song, Y.; Liu, Y.; Yu, P.; Yang, W.; Vajtai, R.; Li, H.; Yuan, S.; Ajayan, P. M., Reversible Formation of g-C₃N₄ 3D Hydrogels through Ionic Liquid Activation: Gelation Behavior and Room-Temperature Gas-Sensing Properties. *Advanced Functional Materials* **2017**, *27* (22), 1700653.
126. Wang, C.; Liu, X.; Wulf, V.; Vazquez-Gonzalez, M.; Fadeev, M.; Willner, I., DNA-Based Hydrogels Loaded with Au Nanoparticles or Au Nanorods: Thermoresponsive Plasmonic Matrices for Shape-Memory, Self-Healing, Controlled Release, and Mechanical Applications. *ACS Nano* **2019**, *13* (3), 3424-3433.

127. Li, Y.; Ma, Y.; Jiao, X.; Li, T.; Lv, Z.; Yang, C. J.; Zhang, X.; Wen, Y., Control of capillary behavior through target-responsive hydrogel permeability alteration for sensitive visual quantitative detection. *Nat Commun* **2019**, *10* (1), 1036.
128. Pahoff, S.; Meinert, C.; Bas, O.; Nguyen, L.; Klein, T. J.; Huttmacher, D. W., Effect of gelatin source and photoinitiator type on chondrocyte redifferentiation in gelatin methacryloyl-based tissue-engineered cartilage constructs. *Journal of Materials Chemistry B* **2019**, *7* (10), 1761-1772.
129. Rose, J. C.; De Laporte, L., Hierarchical Design of Tissue Regenerative Constructs. *Adv Healthc Mater* **2018**, *7* (6), e1701067.
130. Masurier, N.; Tissot, J.-B.; Boukhriss, D.; Jebors, S.; Pinese, C.; Verdié, P.; Amblard, M.; Mehdi, A.; Martinez, J.; Humblot, V.; Subra, G., Site-specific grafting on titanium surfaces with hybrid temporin antibacterial peptides. *Journal of Materials Chemistry B* **2018**, *6* (12), 1782-1790.
131. Li, Z.; Davidson-Rozenfeld, G.; Vazquez-Gonzalez, M.; Fadeev, M.; Zhang, J.; Tian, H.; Willner, I., Multi-triggered Supramolecular DNA/Bipyridinium Dithienylethene Hydrogels Driven by Light, Redox, and Chemical Stimuli for Shape-Memory and Self-Healing Applications. *J Am Chem Soc* **2018**, *140* (50), 17691-17701.
132. Inthavong, W.; Nicolai, T.; Chassenieux, C., Polymer Probe Diffusion in Globular Protein Gels and Aggregate Suspensions. *J Phys Chem B* **2018**, *122* (33), 8075-8081.
133. Shingel, K. I.; Faure, M.-P., Structure-Property Relationships in Poly (ethylene glycol)-Protein Hydrogel Systems Made from Various Proteins. *Biomacromolecules* **2005**, *6* (3), 1635-1641.
134. Patel, A. R., Functional and Engineered Colloids from Edible Materials for Emerging Applications in Designing the Food of the Future. *Advanced Functional Materials* **2018**, 1806809.
135. Qin, X.; Yu, C.; Wei, J.; Li, L.; Zhang, C.; Wu, Q.; Liu, J.; Yao, S. Q.; Huang, W., Rational Design of Nanocarriers for Intracellular Protein Delivery. *Adv Mater* **2019**, *31* (46), e1902791.
136. Guo, H.; Zhang, J.; Xu, T.; Zhang, Z.; Yao, J.; Shao, Z., The robust hydrogel hierarchically assembled from a pH sensitive peptide amphiphile based on silk fibroin. *Biomacromolecules* **2013**, *14* (8), 2733-8.
137. Maslovskis, A.; Guilbaud, J. B.; Grillo, I.; Hodson, N.; Miller, A. F.; Saiani, A., Self-assembling peptide/thermoresponsive polymer composite hydrogels: effect of peptide-polymer interactions on hydrogel properties. *Langmuir* **2014**, *30* (34), 10471-80.
138. Rubert Perez, C. M.; Rank, L. A.; Chmielewski, J., Tuning the thermosensitive properties of hybrid collagen peptide-polymer hydrogels. *Chem Commun (Camb)* **2014**, *50* (60), 8174-6.
139. Um, S. H.; Lee, J. B.; Park, N.; Kwon, S. Y.; Umbach, C. C.; Luo, D., Enzyme-catalysed assembly of DNA hydrogel. *Nat Mater* **2006**, *5* (10), 797-801.
140. Lin, D. C.; Yurke, B.; Langrana, N. A., Mechanical properties of a reversible, DNA-crosslinked polyacrylamide hydrogel. *Journal of biomechanical engineering* **2004**, *126* (1), 104-110.
141. Liu, X.; Zhang, Q.; Gao, G., Bioinspired Adhesive Hydrogels Tackified by Nucleobases. *Advanced Functional Materials* **2017**, *27* (44), 1703132.
142. Zhang, P.; Jiang, J.; Yuan, R.; Zhuo, Y.; Chai, Y., Highly Ordered and Field-Free 3D DNA Nanostructure: The Next Generation of DNA Nanomachine for Rapid Single-Step Sensing. *J Am Chem Soc* **2018**, *140* (30), 9361-9364.

143. Li, M.; Ding, H.; Lin, M.; Yin, F.; Song, L.; Mao, X.; Li, F.; Ge, Z.; Wang, L.; Zuo, X.; Ma, Y.; Fan, C., DNA Framework-Programmed Cell Capture via Topology-Engineered Receptor-Ligand Interactions. *J Am Chem Soc* **2019**, *141* (47), 18910-18915.
144. Tang, H.; Duan, X.; Feng, X.; Liu, L.; Wang, S.; Li, Y.; Zhu, D., Fluorescent DNA-poly(phenylenevinylene) hybrid hydrogels for monitoring drug release. *Chem Commun (Camb)* **2009**, (6), 641-3.
145. Kim, K. K.; Ha, I.; Won, P.; Seo, D. G.; Cho, K. J.; Ko, S. H., Transparent wearable three-dimensional touch by self-generated multiscale structure. *Nat Commun* **2019**, *10* (1), 2582.
146. Hong, Y.; Zhou, F.; Hua, Y.; Zhang, X.; Ni, C.; Pan, D.; Zhang, Y.; Jiang, D.; Yang, L.; Lin, Q.; Zou, Y.; Yu, D.; Arnot, D. E.; Zou, X.; Zhu, L.; Zhang, S.; Ouyang, H., A strongly adhesive hemostatic hydrogel for the repair of arterial and heart bleeds. *Nat Commun* **2019**, *10* (1), 2060.
147. Wirthl, D.; Pichler, R.; Drack, M.; Kettlguber, G.; Moser, R.; Gerstmayr, R.; Hartmann, F.; Bradt, E.; Kaltseis, R.; Siket, C. M.; Schausberger, S. E.; Hild, S.; Bauer, S.; Kaltenbrunner, M., Instant tough bonding of hydrogels for soft machines and electronics. *Science Advances* **2017**, *3* (6), e1700053.
148. Boutry, C. M.; Beker, L.; Kaizawa, Y.; Vassos, C.; Tran, H.; Hinckley, A. C.; Pfattner, R.; Niu, S.; Li, J.; Claverie, J.; Wang, Z.; Chang, J.; Fox, P. M.; Bao, Z., Biodegradable and flexible arterial-pulse sensor for the wireless monitoring of blood flow. *Nat Biomed Eng* **2019**, *3* (1), 47-57.
149. Niu, S.; Matsuhisa, N.; Beker, L.; Li, J.; Wang, S.; Wang, J.; Jiang, Y.; Yan, X.; Yun, Y.; Burnett, W.; Poon, A. S. Y.; Tok, J. B. H.; Chen, X.; Bao, Z., A wireless body area sensor network based on stretchable passive tags. *Nature Electronics* **2019**, *2* (8), 361-368.
150. Li, X.; Yin, Z.; Zhang, X.; Wang, Y.; Wang, D.; Gao, M.; Meng, J.; Wu, J.; You, J., Epitaxial Lifting of Wafer-Scale VO₂ Nanomembranes for Flexible, Ultrasensitive Tactile Sensors. *Advanced Materials Technologies* **2019**, *4* (7), 1800695.
151. Li, J. h.; Chen, J. h.; Xu, F., Sensitive and Wearable Optical Microfiber Sensor for Human Health Monitoring. *Advanced Materials Technologies* **2018**, *3* (12), 1800296.
152. Wang, X.; Liu, Z.; Zhang, T., Flexible Sensing Electronics for Wearable/Attachable Health Monitoring. *Small* **2017**, *13* (25).
153. Liu, H.; Li, M.; Ouyang, C.; Lu, T. J.; Li, F.; Xu, F., Biofriendly, Stretchable, and Reusable Hydrogel Electronics as Wearable Force Sensors. *Small* **2018**, *14* (36), e1801711.
154. Hou, W.; Sheng, N.; Zhang, X.; Luan, Z.; Qi, P.; Lin, M.; Tan, Y.; Xia, Y.; Li, Y.; Sui, K., Design of injectable agar/NaCl/polyacrylamide ionic hydrogels for high performance strain sensors. *Carbohydr Polym* **2019**, *211*, 322-328.
155. Darabi, M. A.; Khosrozadeh, A.; Mbeleck, R.; Liu, Y.; Chang, Q.; Jiang, J.; Cai, J.; Wang, Q.; Luo, G.; Xing, M., Skin-Inspired Multifunctional Autonomic-Intrinsic Conductive Self-Healing Hydrogels with Pressure Sensitivity, Stretchability, and 3D Printability. *Adv Mater* **2017**, *29* (31).
156. Shao, C.; Wang, M.; Meng, L.; Chang, H.; Wang, B.; Xu, F.; Yang, J.; Wan, P., Mussel-Inspired Cellulose Nanocomposite Tough Hydrogels with Synergistic Self-Healing, Adhesive, and Strain-Sensitive Properties. *Chemistry of Materials* **2018**, *30* (9), 3110-3121.
157. Chang, Q.; Darabi, M. A.; Liu, Y.; He, Y.; Zhong, W.; Mequanin, K.; Li, B.; Lu, F.; Xing, M. M. Q., Hydrogels from natural egg white with extraordinary

- stretchability, direct-writing 3D printability and self-healing for fabrication of electronic sensors and actuators. *Journal of Materials Chemistry A* **2019**, *7* (42), 24626-24640.
158. Kang, T. H.; Chang, H.; Choi, D.; Kim, S.; Moon, J.; Lim, J. A.; Lee, K. Y.; Yi, H., Hydrogel-Templated Transfer-Printing of Conductive Nanonetworks for Wearable Sensors on Topographic Flexible Substrates. *Nano Lett* **2019**, *19* (6), 3684-3691.
159. Tai, Y.; Yang, Z., Toward Flexible Wireless Pressure-Sensing Device via Ionic Hydrogel Microsphere for Continuously Mapping Human-Skin Signals. *Advanced Materials Interfaces* **2017**, *4* (20), 1700496.
160. Wang, T.; Yang, H.; Qi, D.; Liu, Z.; Cai, P.; Zhang, H.; Chen, X., Mechano-Based Transductive Sensing for Wearable Healthcare. *Small* **2018**, *14* (11), e1702933.
161. Tian, E.; Wang, J.; Zheng, Y.; Song, Y.; Jiang, L.; Zhu, D., Colorful humidity sensitive photonic crystal hydrogel. *Journal of Materials Chemistry* **2008**, *18* (10), 1116.
162. MacConaghy, K. I.; Geary, C. I.; Kaar, J. L.; Stoykovich, M. P., Photonic crystal kinase biosensor. *J Am Chem Soc* **2014**, *136* (19), 6896-9.
163. Duan, L.; D'Hooge, D. R.; Cardon, L., Recent progress on flexible and stretchable piezoresistive strain sensors: from design to application. *Progress in Materials Science* **2019**, 100617.
164. Jin Young Oh; Donghee Son; Toru Katsumata; Yeongjun Lee; Yeongin Kim; Jeffrey Lopez; Hung-Chin Wu; Jiheong Kang; Joonsuk Park; Xiaodan Gu; Jaewan Mun; Nathan Ging-Ji Wang; Yikai Yin; Wei Cai; Youngjun Yun; Jeffrey B.-H. Tok; Bao, Z., Stretchable self-healable semiconducting polymer film for active-matrix strain-sensing array. *Science Advances* **2019**, *5* (11), eaav3097.