

Self-powered hydrogel sensors

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Abstract: Flexible multimode sensors have attracted increasingly attention due to their excellent mechanical properties, environmental adaptability, sensitivity to electric signals, etc. However, poor self-healing, limited degradability and weak reversible self-adhesion greatly limit the application of flexible sensors composed by rubber, elastomer and other polymers. Although the development of flexible sensors based on hydrogel composites could overcome these limitations, most current hydrogel sensors are mainly driven by external energy sources, which limits their applications. Interestingly, the development of energy conversion technologies paves the way for the design and fabrication of self-powered hydrogel sensors with a continuous energy supply. Herein, we review the self-powering mechanism of hydrogel sensors based on different energy conversion effects. The latest research progress is discussed, focusing on the structural design and corresponding application scenarios of recently developed self-powered hydrogel sensors, including health care, human-computer interaction, and environmental monitoring. Finally, we summarize the current challenges in the field and propose future directions.

Keywords: hydrogels, self-powered, sensors, nanogenerators, photovoltaic effect, hydrovoltaic effect, electromagnetic induction, hybrid power generation

1. Introduction

A very broad range of key technologies, from the development of human-computer interactions, to electronic skin, or medical and environmental monitoring, rely on the fast collection and interpretation of diverse physical and chemical signals. All these applications share some common, challenging requirements. Typically, stable signal collection has to be performed in humid environments for relatively long periods of time. Often, stretchable sensors able to attach to living bodies on wet surfaces that undergo large shape changes are required. In addition, signal collection in the environment or in organisms demand systems that are minimally invasive and biocompatible while retaining a sensitive electrical signal feedback.¹⁻³ They should also be able to operate autonomously as to decrease maintenance costs or work in hard-to-reach locations. In many cases, it is desirable that the sensor itself biodegrades and disappears once its useful life has finished as to avoid costly (and sometimes risky) removal operations. Finally, in large scale applications sensors have to be integrated in arrays able to detect and analyze complex signal patterns.

Most current flexible sensors are usually made out of rubber, elastomers and other polymers, which are limited by their poor self-healing, limited degradation and weak reversible self-adhesiveness in practical application scenarios.⁴ It is necessary to develop new materials that could answer the stringent demands of this growing field. Due to their properties and adaptable chemistry, hydrogels are emerging as promising alternatives in the fabrication of the new generation of flexible sensors.^{5, 6} Hydrogels are "soft and wet" materials composed of three-dimensional (3D) porous polymer cross-linked networks and up to 90% water.⁷⁻⁹ By incorporating functional molecules, different structures and properties can be integrated to endow hydrogels with a variety of structures and properties, including conformability, stretchability, self-healing, adhesion, freeze resistance, biodegradability, biocompatibility, electrical conductivity, etc.¹⁰⁻¹³ In addition, smart, responsive hydrogels can react

under external physical (temperature, electric field, magnetic field, light, pressure and sound) or chemical (pH, composition, concentration and molecular species) stimuli and generate detectable signals through conformational changes.^{14, 15} Although most hydrogels swell in water (and even collapse in some extreme examples), this problem could be solved by introducing chemical cross-links to enhance their strength thereby limiting their swelling ratio.¹⁶ Thus, flexible sensors built from hydrogel composites have been widely researched in fields such as biomedicine, electronic skins, and soft robotics.¹⁷⁻²²

The main limitation of most current hydrogel-based flexible sensors is their dependence on external power sources (i.e. batteries) for their daily operation. These energy storage devices have limited capacity and are harmful to the environment. In addition, they hamper miniaturization, which severely limits the lifetime and application scenarios.^{23, 24} Over the past few years, a considerable effort has been devoted to the development of self-powered hydrogel sensors that are renewable, sustainable, environmentally friendly, and cost-effective.^{23, 24} Among them, nanogenerators (NGs) are an ideal alternative to conventional power supply technologies. They can efficiently harvest various sources of energy (i.e. kinetic energy from raindrops, mechanical energy from movement, thermal energy from the operation of machines, etc.) and convert them into electrical energy.^{25, 26} Therefore, the construction of self-powered structures based on nanogenerators in hydrogels can not only effectively avoid the additional economic burden and environmental problems caused by the regular replacement of batteries, but also broaden the application scenarios of flexible hydrogel electronics (**Figure 1**).^{25, 27-30} In addition, self-powered sensors could facilitate the implementation of sensor arrays to monitor complex behavior patterns from body movement to weather or contaminant distribution in large areas. Their autonomy can diminish maintenance costs and facilitate their use in hard-to-reach conditions.

During the past three years, the research in self-powered hydrogel sensors based on triboelectric nanogenerators (TENGs) and piezoelectric nanogenerators (PENGs) has been the most comprehensive.^{21, 31} Power generation based on triboelectric effects combines the two phenomena of contact electrification and electrostatic induction, which can effectively convert mechanical energy generated by the environment and human motion into electrical energy. This energy conversion has the advantages of low cost, easy preparation, lightweight, high portability and eco-friendliness.³² The other typical example of self-powered hydrogel sensors rely on nano-piezoelectric materials to convert irregular and weak mechanical energy into electrical energy, which has the advantages of high-output performance, small size, easy processing, high flexibility, adaptability, etc.³³ In addition, new self-powered hydrogel sensors based on pyroelectric (PyNG) and thermoelectric generators (TEG), the photovoltaic or hydrovoltaic effects and electromagnetic induction are also receiving increasing attention.^{21, 34, 35} Although great progress has been made based on these different powering effects, self-powered hydrogel sensors based on a single source still suffer from low output currents, low output voltage and limitations in energy harvesting scenarios.^{22, 31} Accordingly, researchers have further developed self-powered hydrogel sensors with hybrid powering effects by combining multiple energy harvesting mechanisms to improve energy utilization and environmental adaptability.³⁶⁻³⁸

In this review, we first introduce the energy conversion mechanisms that can be used in self-powered sensing systems, mainly focusing on the power generating mechanisms of NGs (PENGs, TENGs and PyNG/TEG), photovoltaic effect, hydrovoltaic effect, electromagnetic induction, and hybrid power generation effects. Then, the applications of self-powered hydrogel sensors based on these powering mechanisms are considered, including mechanical sensing, healthcare, and environmental monitoring. Finally, the current challenges of self-powered hydrogel sensors are discussed and future development

trends and research directions are proposed.

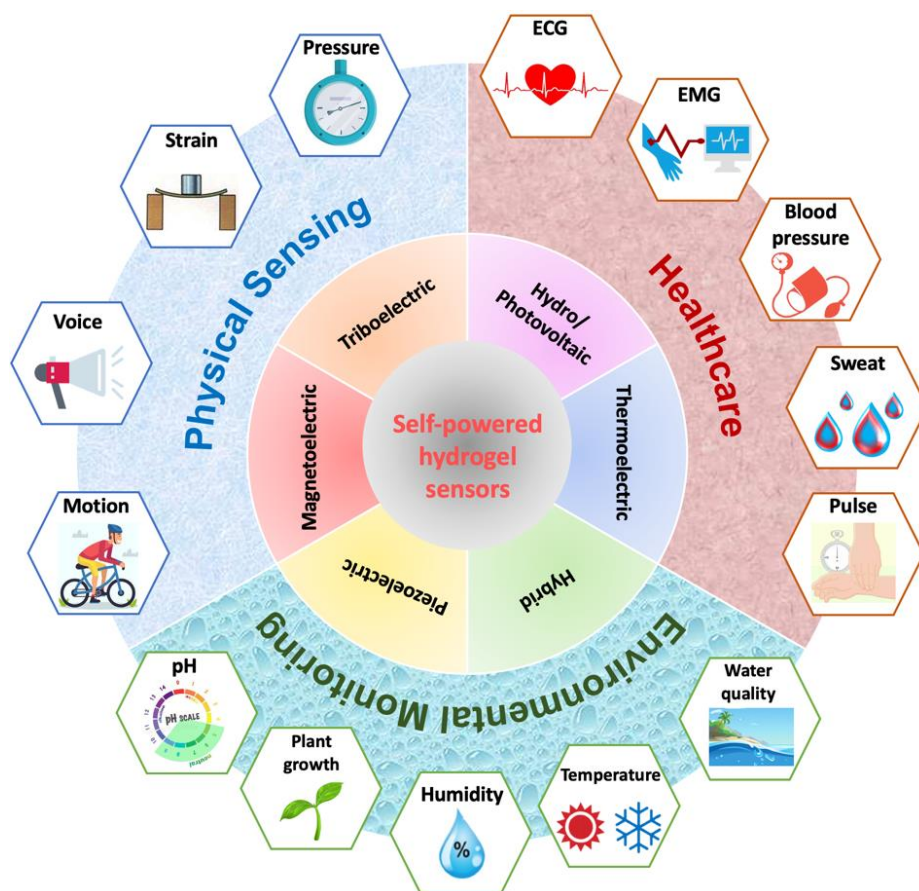


Figure 1. Summary of self-powered hydrogel sensors.

From the power generation mechanism to the entire self-powered hydrogel sensor system, from single to hybrid energy conversion effects in hydrogel sensing systems, including physical sensing, healthcare and environmental monitoring in view of applications.

2. Self-powering mechanisms

An in-depth understanding of the power generation mechanism is crucial for the design of relevant self-powered hydrogel electronic devices with improved performance. To date, researchers have developed various energy conversion technologies based on piezoelectric, triboelectric, thermoelectric, magnetoelectric, photovoltaic, hydrovoltaic, and a combination of two or more of these energy conversion effects to successfully transform mechanical, thermal, magnetic, solar or chemical energies into electricity. The specific working mechanisms of these self-powered energy harvesters are

described below.

2.1 Power generation based on nanogenerators

Nanogenerator-based self-powered hydrogels refer to those hydrogel sensors with nanogenerator structures, which mainly contain triboelectric nanogenerators, piezoelectric nanogenerators, pyroelectric nanogenerators/ thermoelectric generators and hybrid nanogenerators (HNG). The power generation mechanism of these nanogenerators will be discussed in detail as following.

2.1.1 Triboelectric nanogenerator (triboelectric effect)

The encounter of two dissimilar materials would result in contact electrification, often referred to as triboelectrification. The energy harvesting of TENG combines the phenomena of triboelectrification and electrostatic induction between two triboelectric layers. It can convert efficiently the mechanical energy in the environment into valuable electrical energy.^{21, 31, 39} Before two materials with different electronegativity come into contact, electrons cannot be transferred due to the local trapping effect of the potential well. However, when the friction surfaces touch, the single potential well becomes an asymmetric double potential well due to the overlap of the electron clouds, and electrons will transfer between the two materials. Electrons in atoms with low electronegativity tend to jump towards the atoms with high electronegativity. When the two are separated, the transferred electrons will remain in the low-electronegativity material due to the energy barrier, and the two frictional surfaces will be charged with opposite signs. When these surfaces are separated under the further action of an external force at room temperature, the charge generated by friction will cause a potential drop between the two frictional surfaces, and the potential drop will change with their contact and separation. To balance the above potential difference, free electrons will flow back and forth through the external circuit, and this

alternating flow of electrons realizes the output of the corresponding current. It should be noted that when two materials are separated at high temperature, electrons are more likely to jump out of the potential well and eventually return to the original material atoms or be emitted into the air.⁴⁰ The generated charge can be retained by the material for hours at room temperature in the form of an electrostatic charge. According to the device structure and working mode, TENGs can be divided into the following four different basic operation modes (**Figure 2A**): lateral sliding (LS), vertical contact-separation (CS), single-electrode (SE) and free-standing triboelectric layer (FT). Among them, LS and CS have opposite friction directions but the same compositional configuration, that is, upper and lower conductive layers (electrodes) and dielectric layers (friction layers). The CS mode relies on the relative motion between the two triboelectric layers perpendicular to the interface, while the LS mode relies on the relative displacement of the triboelectric layers in a direction parallel to the interface. SE, on the other hand, has only one electrode and one triboelectric layer, the contact electrification occurs when an external object comes into contact with the triboelectric layer. FT typically generates a current output by rubbing a dielectric layer against two interconnected conductive layers underneath it. The structural characteristics, strengths and weaknesses, as well as application scenarios of these four different working modes are shown in **Table 1**.³⁹

Table 1. Characteristics of the four operating modes of TENGs.³⁹

Modes	Structural features	Advantages	Disadvantages	Applicable occasions
LS	Horizontal/rotational movement, almost without a gap	High frequency, continuous and high electricity output	Easy damage of friction surface, poor long-term stability	Rotational and air/water flow energy harvesting
CS	Vertical movement, a large gap existed	High output voltage	Pulse output	Pressing, impacting, bending, sharking, vibration

SE	Only one electrode, another electrode is ground	Simple, versatile in harvesting energy, easy for integration and to carry	Relatively low output and signal instability	Sliding/typing/touching the screen
FT	Multiple forms of movements, symmetric electrodes, asymmetric charge distribution	High energy conversion efficiency	Inconvenient to move due to fixed electrodes, complex for integration	Rotational and vibration energy harvesting

2.1.2 Piezoelectric nanogenerator (piezoelectric effect)

PENG works by effectively converting mechanical energy (strain or stress) into electrical energy through the piezoelectric effect, thereby enabling energy harvesting.⁴⁰ The basic structure of PENGs consists of three layers, namely the upper and lower electrode layers and the middle piezoelectric material layer (Figure 2B). Under the action of an external force (direct piezoelectric effect) or an applied electric field (reverse piezoelectric effect), the piezoelectric material in the middle layer undergoes mechanical deformation, resulting in negative strain. When the piezoelectric material is electrically neutral, this deformation will cause the positive and negative charge centers of the material to shift, resulting in internal electrical polarization of the material. Corresponding bulk and surface charges, and charges of opposite polarity appear on both sides of the piezoelectric material. On opposite surfaces, a potential drop is induced across the electrodes to reach a new equilibrium state. When connected to an external load, this piezoelectric potential drives electrons through the external circuit to output power.⁴¹ After releasing the external force, the electrons flow back to return to the initial state, resulting in the reverse piezoelectric current generation. By periodically changing the magnitude and direction of the applied external force, the magnitude and direction of the induced piezoelectric potential will also change periodically, which helps the external circuit to achieve the

continuous output of alternating current.⁴² The key feature of piezoelectric materials is the piezoelectric coefficient, the higher the piezoelectric coefficient, the higher the energy conversion efficiency.²¹ With a fixed strain rate and device area, high-output PENGs can be achieved by adopting piezoelectric materials with a high piezoelectric coefficient and optimizing the design structure of flexible substrates.

2.1.3 Pyroelectric nanogenerator (PyNG)/ Thermoelectric generator (TEG) (pyroelectric effect)

The working mechanism of PyNG/TEG includes the primary/secondary pyroelectric effect, the difference is that the former refers to the charge generated by the temperature difference under constant strain, while the latter relies on the strain caused by thermal expansion to generate a piezoelectric potential difference.⁴³ The pyroelectric effect mainly relies on the spin Seebeck effect to convert thermal into electrical energy (Figure 2C). The voltage difference that forms between two places of a conducting material when their temperatures differ is referred to as the Seebeck effect. At its core is the positive variation of the energy of the carriers in a conductor with temperature, the higher the temperature the greater the kinetic energy of the carriers.⁴⁴ When there is a difference in temperature between the two ends of the conductor at the joint (ΔT), the carriers at the hot end move towards the cold end and accumulate there until the concentration distribution of carriers reaches equilibrium. At this point, a corresponding electric potential (ΔV) is generated at both ends of the conductor that drives the directional movement of electrons in the external circuit, thus acting as an energy supply. Therefore, we can use the temperature difference between the human body and the environment to develop PyNGs that can convert body heat into electrical energy, allowing them to serve as a power source for medical information sensors.

2.2 Power generation based on photovoltaic effect

In 1954, Fahrenbruch et. al invented the first high-power modern silicon solar cell, in which photoexcited carriers are separated by a built-in electric field generated at the P-N junction.⁴⁵ As the core component of a solar cell, the photovoltaic effect of the P-N junction can effectively convert solar energy into electrical energy.⁴⁶ As shown in Figure 2D, at the P-N junction interface, there are a large number of free electrons on the N-type semiconductor side that can diffuse into the P-type semiconductor, while there are a large number of holes that can diffuse into the N-type semiconductor in the P-type semiconductor. This diffusion process causes the N-type semiconductor at the interface to be positively charged and the P-type semiconductor to be negatively charged, thus creating a built-in electric field from the N-type semiconductor to the P-type semiconductor at the P-N junction interface. Electron-hole pairs will form at the P-N junction interface when the device is exposed to sunlight. In the presence of the built-in electric field, electrons migrate towards the N-type semiconductor and holes migrate towards the P-type semiconductor until the photogenerated electric field generated by the accumulation of electrons and holes in the N-type and P-type semiconductors respectively can counteract the built-in electric field. In this case, the N-type and P-type semiconductors are negatively and positively charged separately, and a potential difference is formed at the P-N junction, allowing the flow of free electrons in the external circuit. It is noticeable that the photovoltage of P-N junction based photovoltaic cells is limited by the bandgap energy of the constituent semiconductors and the ultimate efficiency is limited by the Shockley-Queisser (S-Q) limit.⁴⁷ Another famous photovoltaic effect is achieved by ferroelectric materials, which is also called bulk photovoltaic (BPV) effect.⁴⁸ For example, a homogeneous ferroelectric material could generate an short-circuit current (ISC) at zero bias when it was under uniform illumination, and produce an unusually large photovoltage far exceeding its bandgap energy. This peculiar photovoltaic effect

originates from the asymmetric distribution of photoexcited non-equilibrium carriers in the momentum space which caused by the absence of central symmetry in the material.⁴⁹ Due to the unique charge separation mechanism, solar cells based on the BPV effect can exceed the S-Q limit in principle.⁵⁰

2.3 Power generation based on hydrovoltaic effect

As an emerging technology, the hydrovoltaic effect could generate electricity by the direct interaction of material with water droplets.²⁵ Hydrovoltaic power generation usually relies on the dynamic distribution of ions in the electric double layer.³⁴ As shown in Figure 2E, during the movement of an ion droplet (droplet containing ions in solution) along the solid surface, the ions between the solid-liquid interface will be redistributed, and pseudo-capacitances (denoted C_F and C_R respectively) are formed at the front and rear ends of the solid-liquid interface, resulting in a charging/discharging process. The potential generated by this process corresponding to the moving boundary $L(dL/dt)$ mode is also referred to as the pulling potential. For example, the equivalent current of an ionic droplet moving with velocity v on a conductive solid surface can be expressed as⁵¹

$$I = \frac{dq_e}{dt} = \varphi \frac{dC_F}{dt} = -\varphi \frac{dC_R}{dt} = \varphi W C_o \frac{dL}{dt}$$

where φ is the surface potential relative to the Stern layer, C_o is the pseudo-capacitance per unit area, W is the width of the conductive solid surface under the droplet, and L is the distance travelled by the droplet.

The mechanism corresponding to a droplet impacting an electret film to generate electricity is derived from the droplet dynamics of the resistor-capacitor (RC) circuit, where the dynamic double-layer capacitance varies as a function of the derivative area of the diffusing droplet (dS/dt) and the corresponding induced current can be quantified as^{52, 53}

$$I = \frac{dq_e}{dt} = \sigma \frac{dS}{dt}$$

where σ is the surface charge density of the solid and S is the area of the droplet.

For example, if a NaCl-containing water droplet was dropped on a graphene, the charges within the droplet are distributed symmetrically and no potential difference is generated.⁵⁴ Once the droplet starts moving, the accumulation of cations at the front boundary of the water-graphene interface would draw electrons from the graphene. Meanwhile, electrons at the back boundary would be released into graphene after ion desorption. The charging of the front edge and the discharge of the back edge could generate voltages of a few millivolts across the graphene along the direction of the droplet's movement. Interestingly, the voltage generated exhibits a linear dependence on the droplet velocity, in agreement with hydrovoltaic effect theory.⁵¹ In addition, the output voltage of graphene can also be tuned by changing the number of droplets or the concentration of ions in the droplets.⁵⁵

2.4 Power generation based on electromagnetic induction

The power harvesting mechanism of the magnetoelectric effect is mainly based on the phenomenon of electromagnetic induction, which is aroused by the relative movement between magnets and conductive wires. Since its first discovery by Faraday in 1831, this phenomenon has gradually become the main source of electricity for human society, as energy from fossil fuels, water, wind and nuclear, etc. can all be converted into electricity through electromagnetic induction.³⁵ However, traditional electromagnetic sensing devices usually adopt rigid magnets, which are incompatible with flexible hydrogel sensors.⁵⁶ To address this problem, magnetic powders are dispersed in polymer elastomers to fabricate composites with reduced stiffness that can be used in the fabrication of a new generation of self-powered soft electronic devices. In addition to the magnetic powders, conductive helices would

be embedded in the elastomer to achieve anisotropic electromechanical switching and realize self-powering (Figure 2F).³⁵ Unlike the conventional piezoelectric concept, the mechanical force applied to the flexible sensor affects the electrical output using the magnetoelectric effect achieved by changing the relative position between the magnetic powder and the conducting helix. The corresponding output voltage can be expressed as:³⁵

$$E(V) = -N \frac{\Delta\Phi}{\Delta t} = -\sum_{i=1}^N \frac{\Delta\Phi_i}{\Delta t} = -\sum_{i=1}^N \frac{\Phi_i(after) - \Phi_i(before)}{\Delta t}$$

Where $E(V)$ is the output voltage, N is the number of helical layers, $\Delta\Phi$ is the total magnetic flux change, $\Delta\Phi_i$ is the magnetic flux change of each equivalent ring, and Δt is the compression time of the composite elastomers. The electromechanical conversion performance can be improved by adjusting the powder content, the number of conductive helix layers, the compression speed and other factors.³⁵

2.5 Hybrid power generation

As mentioned previously, self-powered hydrogel sensors based on a single energy conversion effect usually suffer from low output currents/voltages, and limitations in complex energy harvesting scenarios.^{22, 31} For instance, hydrogel sensors that rely on a photovoltaic structure to generate power for the sensing system lose their intended functions in dark conditions. The TENG/PENG, which is based on the conversion of mechanical energy, faces similar problems. The amount of energy that can be collected by the sensor to function as an energy supply unit is frequently insufficient if it is attached to a location where there is a small change in motion. To solve this problem, researchers have started to construct hybrid energy harvesting structures in hydrogel sensors to increase their efficiency while extending their working environments. These systems can be divided into those that use hybrid

nanogenerators (HNG) and those that apply hybrid power generation. The former usually refers to systems combining different NGs such as tribo-piezoelectric hybrid NGs and tribo-piezoelectric-pyroelectric hybrid NGs,^{57, 58} while the latter usually cover energy harvesting structures that use of additional energy conversion effects together with nanogenerators, for example PENG or TENG together with photovoltaic generation.

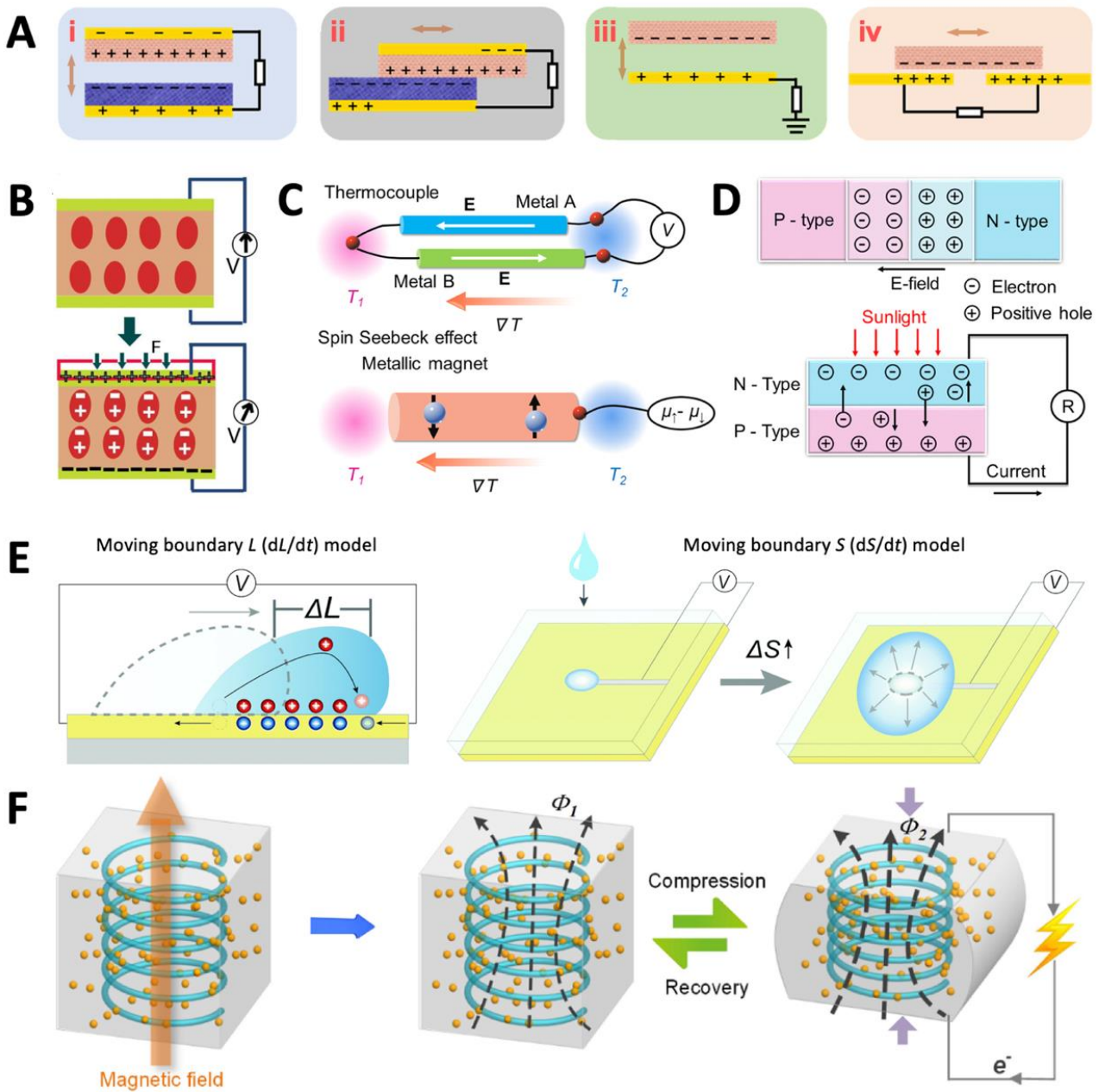


Figure 2. Different self-powering mechanisms.

(A) Four typical working modes of TENG. i.e. (i) vertical contact-separation mode, (ii) contact-sliding

- mode, (iii) single-electrode mode, and (iv) freestanding triboelectric layer mode. Reproduced with permission from Dong et al.⁵⁹ Copyright 2021, Springer Nature.
- (B) Schematic illustration of PENG. Reproduced with permission from Xu et al.⁴⁰ Copyright 2018, MDPI.
- (C) Schematic illustration of PyNG/TEG. Reproduced with permission from Zhao et al.²¹ Copyright 2020, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
- (D) Schematic illustration of photovoltaic effect. Reproduced with permission from Zhao et al.²¹ Copyright 2020, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
- (E) Schematic illustration of hydrovoltaic effect. Reproduced with permission from Wang et al.³⁴ Copyright 2022, American Chemical Society.
- (F) Schematic illustration of magnetoelectric effect. Reproduced with permission from Zhang et al.³⁵ Copyright 2020, Elsevier BV.

3. Applications of self-powered hydrogel sensors

Numerous hydrogel sensors with various self-powered mechanisms have been created based on the energy harvesting technologies mentioned above and are applied in the fields of mechanical sensing, health care, and environmental monitoring. They not only avoid the financial burden and environmental problems caused by regular battery replacement, but also recycle energy that would otherwise not be used, effectively alleviating the current energy crisis and reducing environmental pollution.

3.1 Physical Sensing

Hydrogels are made of a polymer network and water molecules, the former endows them with elastomeric properties, and the latter gives them ionic conductivity and the ability to transmit high-frequency electric signals over long distances. The water molecules in the hydrogel can have similar physical and chemical properties to liquid water as the mesh size of the polymer network (10 nm) is much larger than their size and they can move freely inside.⁶⁰ The conductivity of the hydrogel can therefore be adjusted by adding soluble salts (LiCl, NaCl, KCl, MgCl₂, K₂SO₄, etc.). A mechanically responsive, adhesive, self-powered hydrogel sensor can sense various external stimuli (stretching,

compression) and feedback them in the form of electric signals.⁶¹ For example, when a hydrogel sensor undergoes tension/compression, the corresponding resistance/capacitance increases non-linearly upward with strain/pressure (**Figure 3A, 3B**). Additionally, self-powered hydrogel sensors can adhere directly to the human epidermis and move with the body (Figure 3C). These sensors are therefore widely used in biomechanical sensing and monitoring of physical parameters including breathing, joint flexion, throat vibrations and pulse (Figure 3D).⁶²⁻⁶⁸

Based on the physical sensing properties of self-powered hydrogel sensors, Guo et al. further developed a TENG-based self-powered agar-hydrogel sensor that can be used for all-round infant movement monitoring and provide real-time early warnings.⁶⁹ This agar hydrogel-based sensor resembles a sandwiched structure consisting of gelatin, agar hydrogel, and seaweed, where the agar hydrogel acts as the electrode layer, and seaweed is sandwiched between the other two layers so as to protect the gelatin from water erosion.⁶⁹ By attaching these sensors to different parts of the infant's body, the researchers have established an area sensor network to capture and collect electrical impulse signals linked to specific movements. Relying on the different characteristics of these signals, a deep learning algorithm was used to identify the infant's movement patterns quickly and accurately (Figure 3E). The corresponding learning accuracy, learning rate, and loss function indicate the reliability and efficiency of this algorithm (Figure 3F). The motion signal identified by the deep learning algorithm can be wirelessly transmitted to the guardian's mobile phone for remote monitoring. This intelligent system provides a paradigm for baby care in the Internet of Things era and illustrate an approach based on the integration of self-powered sensors in intelligent networks that could be used to monitor and identify complex behavior patterns with the help of artificial intelligence.

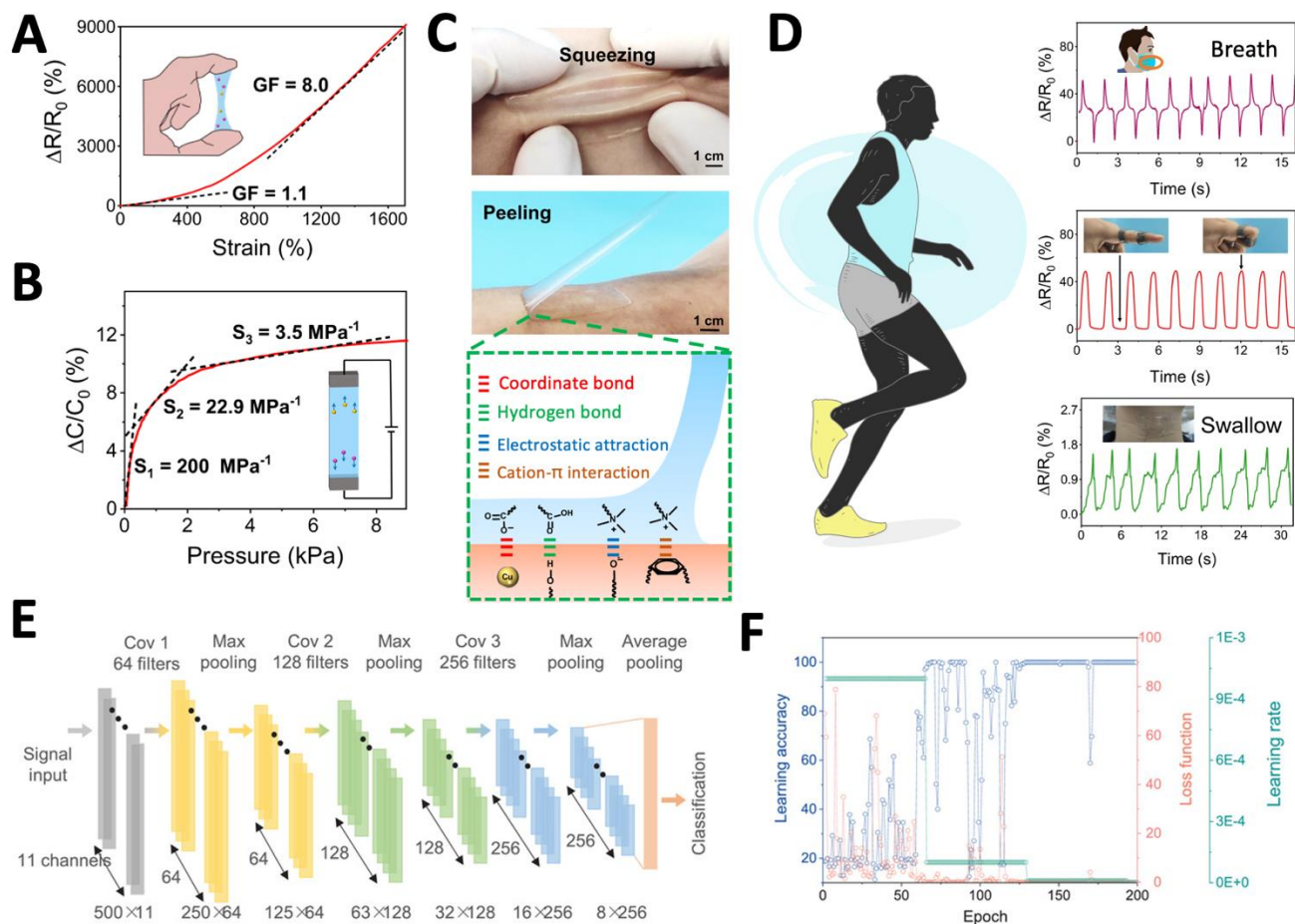


Figure 3. Physical sensing properties of self-powered hydrogels and their applications.

- (A) Strain-dependent resistance changes of typical hydrogel sensors. Reproduced with permission from Zhang et al.⁶¹ Copyright 2021, Springer Nature.
- (B) Pressure-dependent capacitance variations of typical hydrogel sensors. Reproduced with permission from Zhang et al.⁶¹ Copyright 2021, Springer Nature.
- (C) Mechanically compliant and adhesive to human skin properties of typical hydrogel sensors. Reproduced with permission from Zhang et al.⁶¹ Copyright 2021, Springer Nature.
- (D) Self-powered hydrogel sensors for biomechanical sensing. Reproduced with permission from Zhang et al.⁶¹ Copyright 2021, Springer Nature.
- (E) The architecture of deep learning algorithms for identifying baby movement patterns. Reproduced with permission from Guo et al.⁶⁹ Copyright 2022, Wiley-Blackwell.
- (F) Classification accuracy, learning rate and loss function of the deep learning algorithm at 200 epochs. Reproduced with permission from Guo et al.⁶⁹ Copyright 2022, Wiley-Blackwell.

3.2 Healthcare

The iontronic of hydrogels primarily relies on non-Faraday processes in which no matter or charge crosses the interface.⁶⁰ Hydrogels are solid, unlike liquid aqueous electrolytes, and can be attached

directly to ionic devices or living tissues to transmit electric signals.⁷⁰ As a result, hydrogel sensors have also been used to measure human electrophysiological signals such as electromyogram (EMG), electrocardiogram (ECG), and electroencephalogram (EEG), which are crucial for the diagnosis and prediction of heart, muscle and nerve-related diseases (**Figure 4A**).^{71, 72}

In addition to the detection of electrophysiological signals for heart, muscle or nerve-related diseases, self-powered hydrogel sensors can also be used to spot and prevent diseases such as cystic fibrosis by detecting soluble biomarkers including electrolytes or metabolites in sweat. For example, a TOCNF/PANI-PVAB hydrogel enclosed by polydimethylsiloxane (PDMS) and an ion-selective membrane (ISM) was assembled by Qin et al. to create a self-powered hydrogel sweat sensor with excellent stretchability and self-healing properties (Figure 4B).⁷³ The hydrogel electrode inside is prepared through the *in situ* polymerization of cellulose nanocomposites and polyaniline, as well as the crosslinking with polyvinyl alcohol/borax. This hydrogel composite sensor is capable of detecting Na^+ , K^+ , and Ca^{2+} concentrations in human sweat in real time with the high selectivity and sensitivity required for health monitoring. In the future, these sensors could combine the detection of physical (e.g. movement or electrical) and chemical signals to provide, fast, comprehensive assessments.

Human-machine interaction (HMI) between patients, healthcare providers, and medical equipment plays a vital role in intelligent healthcare systems. These systems could not only assist in meeting patients' medical needs, but also provide medical personnel with the appropriate support. For example, Yang et. al showed how a sandwich structure triboelectric nanogenerator can power a miniature sensor part of an intelligent medical monitoring system able to alert a caretaker when a patient bends their finger (Figure 4C).²⁷ This sensor is based on a transparent and stretchable polyvinyl alcohol/phytic

acid (PVA/PA) hydrogel with excellent mechanical and electrical properties. Like in the baby monitoring example in the previous section, this work illustrates the possibilities that could be opened by combining fast sensing with the use of artificial intelligence for signal interpretation. The work not only demonstrates the value of TENG-based self-powered hydrogel sensors for medical HMI applications, but also points out the direction for the development of self-powered hydrogel sensors in the field of brain-computer interfaces.

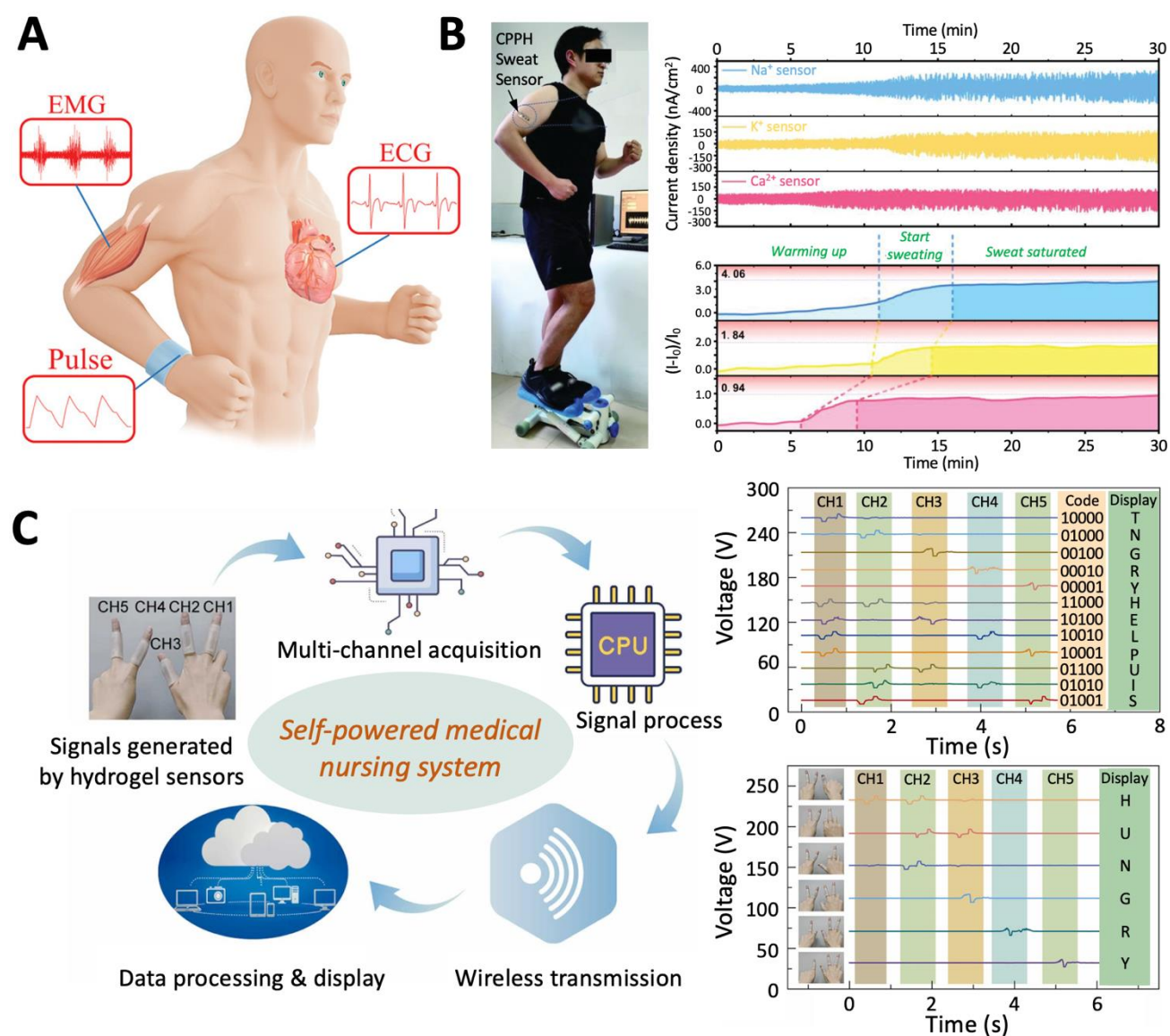


Figure 4. Applications of self-powered hydrogels in the field of healthcare.

(A) Self-powered hydrogel sensors for human electrophysiological signals monitoring. Reproduced with permission from Li et al.⁷⁴ Copyright 2022, Wiley-Blackwell.

- (B) Self-powered hydrogel sensors for human sweat analysis. TOCNF: 2,2,6,6-tetramethylpiperidine-1-oxyl radical oxidized CNFs; PANI: polyaniline; PVAB: PVA/borax; PVA: polyvinyl alcohol. Reproduced with permission from Qin et al.⁷³ Copyright 2022, Wiley-Blackwell.
- (C) Self-powered hydrogel sensors for promoting human-machine interaction in nursing and patient safety. Reproduced with permission from Yang et al.²⁷ Copyright 2022, Elsevier BV.

3.3 Environmental Monitoring

Human beings are placing a greater emphasis on green development to improve the living environment. Temperature, humidity and pollutant levels are key factors affecting the living conditions. Therefore, it is necessary to track these variables and understand their evolution in order to prevent pollution and climate change and safeguard food security. In this respect, self-powered hydrogel sensors pave the way for large scale monitoring networks at a very low emission cost.

Temperature and humidity can directly affect our perception of environmental comfort and we need to monitor and understand their changes. However, the majority of temperature and humidity sensors currently available on the market require an external power source to operate, which is a barrier to their use in a decarbonized, energy-saving society. In order to reduce energy consumption, Xia et al. constructed a hydrogel-based gradient polyelectrolyte membrane (GPM) self-powered hydrogel sensor, of which the energy supply primarily relied on the harvesting of chemical energy during the selective unidirectional permeation of ions through the GPM membrane.⁷⁵ This hydrogel-based GPMs were prepared by a hydrogel-assisted reaction-diffusion method, where the polyacrylamide hydrogel was first submerged into a concentrated low-molecular-weight polycation solution to form a polycation-rich hydrogel container, and then immersed into a high-molecular-weight polyanion solution to form a thin complex layer based on the strong electrostatic complexation. The as-prepared sensor could exhibit a thermo-responsive self-sensing potential under hydration and a humidity-sensitive

transmembrane potential under dehydration/dryness, thus providing reliable and accurate feedback of the temperature and humidity changes of its environment. **(Figure 5A)**. This work provides a path for the future development of self-powered systems with multiple sensing capabilities.

Large quantities of synthetic chemical fertilizers are usually consumed in agricultural production, which not only reduces economic benefits but also increases the emission of greenhouse gasses.⁷⁶ To address this problem, Hsu et. al fabricated a self-powered lightweight fertilization system based on a PAA-RGO-PANI dual network hydrogel sensor through inductively coupled plasma etching.⁷⁷ The versatile polyacrylic acid hydrogel is prepared through chemical cross-linking of acrylic acid molecules (diluted by RGO solution) with the help of N-N' methylenebisacrylamid agent, and further coated with polyaniline to increase conductivity. This system converts the mechanical energy in the environment (airflow, rain, sound) into electrical energy through the triboelectric nanogenerator structure in the sensor. The harvested electrical energy could be used to monitor and promote plant growth in real time (the latter by providing LED light a "light fertilizer") and to follow ammonium concentration (Figure 5B). This work demonstrates that self-powered hydrogel sensors exhibit great potential in the construction of efficient and sustainable green intelligent agricultural systems and that , like in the case of healthcare, the combination of physical and chemical sensing can open new application opportunities. /

Sulfur dioxide (SO₂) is a gaseous pollutant that is extremely harmful to human health and the environment.^{78, 79} Therefore, rapid and accurate detection of SO₂ content in the air is of great significance for preventing secondary pollution such as acid rain. However, most current SO₂ sensors require an external energy supply, and some sensors even require high-temperature conditions for

effective detection, resulting in very high energy consumption. To address these issues, Wang et. al developed a self-powered MXene/TiO₂/SnSe hydrogel sensor driven by ocean wave energy based on the liquid-solid TENG energy conversion effect, for the detection of SO₂ gas content in the air.⁸⁰ The hydrogel electrode inside is prepared through the physical crosslinking among PVA molecules, ethylene glycol and conductive ions. As shown in Figure 5C, the sensor could not only sensitively monitor the level of SO₂ but also simultaneously detect the air temperature and humidity, and the height of the seawater. This work provides ideas for the development of self-powered hydrogel sensors for marine environmental monitoring based on the liquid-solid TENG energy conversion effect. Following this research, we can further develop self-powered hydrogel sensors for detecting seawater quality (i.e., heavy metal ion content, seawater pH, concentration of N and P, etc.).

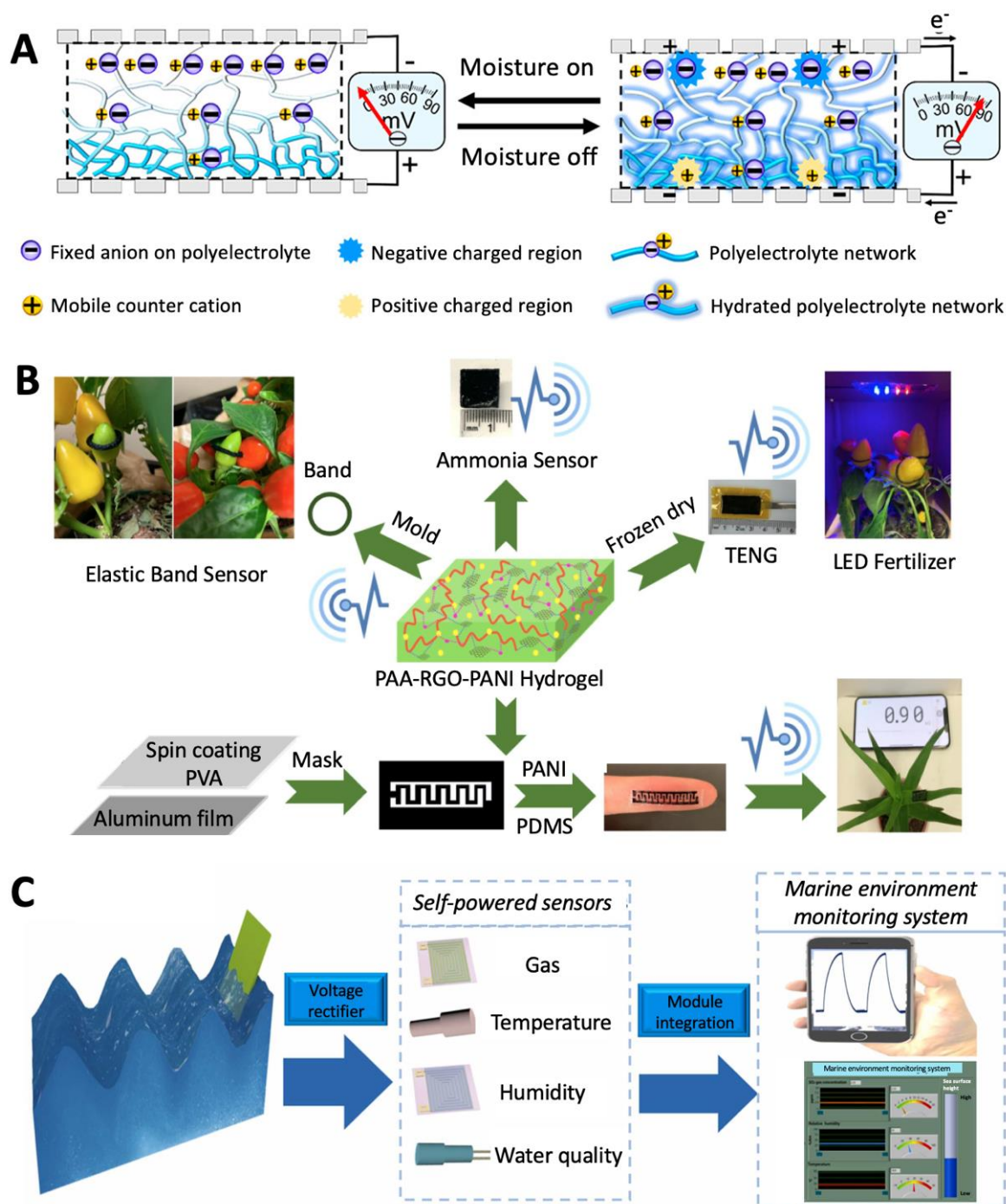


Figure 5. Applications of self-powered hydrogels in the field of environmental monitoring.

(A) Self-powered hydrogel sensors for environmental temperature and humidity sensing. Reproduced with permission from Xia et al.⁷⁵ Copyright 2022, American Chemical Society.

(B) Self-powered hydrogel sensors for promoting and monitoring plant growth in smart farming. PAA: poly acrylic acid; RGO: reduced graphene oxide; PANI: polyaniline. Reproduced with permission from Hsu et al.⁷⁷ Copyright 2021, Elsevier BV.

(C) Self-powered hydrogel sensors for marine environmental monitoring. Reproduced with permission from Hsu et al.⁸⁰ Copyright 2022, Elsevier BV.

4. Conclusion & Perspective

This perspective follows the progress of self-powered hydrogel sensors, from theory to practical applications and recent developments. Over the past few years, great advances have been made in the conversion of kinetic, thermal and chemical energies into electricity. The use of this technology to recover energy lost in daily life to power devices is extremely appealing. It not only eliminates the need for external power sources, but also effectively recycles energy that would otherwise be wasted. We have shown several examples, including the conversion of mechanical and thermal energy from human movement; chemical energy from sweat; solar, magnetic, wind, and wave energies from the environment into electrical energy. However, there are still some challenges in large-scale production and application, and room for the development of new technologies (**Figure 6**).

First, the challenge faced by most self-powered hydrogel sensors is the single energy harvesting source, which severely limits their application. Although the construction of hybrid power generation structures is the prevailing trend, it has limitations. For example, in existing hydrogel sensors, the combination of different power generation effects is often simply stacked, which improves the overall energy harvesting capacity but reduces the energy harvesting efficiency of each single nano-generating structure inside. Additionally, the superposition of multiple energy conversion effects would increase the number of materials used and the complexity of the structure, which is not conducive to device miniaturization. To enhance harvesting efficiency and broaden the application scenarios, researchers should figure out how to reduce the space required for power generation devices by adjusting their chemical composition and optimizing the overall structural design.

Second, it's crucial to consider other properties like biocompatibility, implantability, wet adhesion,

stretchability, flexibility, and degradability when designing self-powered hydrogel sensors for health monitoring. These sensors can be divided into *internal and external* depending on the body location. The former are typically used to collect information from various bodily organs, including the aorta, lungs, stomach, and heart, etc. to keep tabs on the user's health. For example, medical signals such as endocardial pressure and arrhythmias can effectively provide timely clues for the detection of cardiovascular diseases such as ventricular fibrillation and premature ventricular contractions.²¹ Generally, this type of self-powered sensor needs to be both implantable and biocompatible. A significant challenge is how to effectively improve their biosafety, interference resistance, and miniaturization. In this regard, waterproofing and miniaturization of the sensor's functional structures such as energy supply, sensing, signal transmission, through a reasonable layout device is an important area of development. Biodegradability also restricts the commercialization of internal short time monitoring self-powered hydrogel sensors for biomedical or implantable applications. For example, some implantable devices are used for short-term monitoring after an operation, and they have to be removed by surgery after the patient recovers, which makes the patient need to go through the painful process again. Therefore, how to construct self-powered hydrogel sensors with biodegradable materials while retaining their corresponding functions is also an issue to be addressed in future research. External sensors, which frequently need to be both stretchable and flexible, are used to collect signals such as sweat, pulse, body temperature, respiration, sound, and body movement. The moisture retention, structural stability, and electric signal stability of hydrogel sensors are important factors to be considered due to long-term exposure to air and repetitive mechanical motions when monitoring limb movements. The weak and unstable adhesion of hydrogels to wet surfaces can result in interfacial failure and subsequent loss of functionality, which seriously hinders their applications. Therefore, it is

necessary to develop robust wet adhesion. Here, the study of natural structures could provide useful design guidelines. For example, organisms such as clingfishs, tree frogs, octopus etc., achieve underwater adhesion through the suction of adhesion cups and the friction of the micro-nanostructures on its surface.⁸¹

Last but not least, the stability or long-term durability of self-powered hydrogel sensors should be further investigated and improved. In practice, hydrogel sensors are often limited by factors such as device structure, mechanical strength of component materials, wear of triboelectric layer materials, weak connections between electrodes, and moisture/temperature in the environment.⁸² It is necessary to improve the stability and lifetime of the sensors through the optimization of their structural design/components, the use of new triboelectric polymer layers, the design of strong interfacial bonding structures, and testing in multiple pre-defined environments. For self-powered hydrogel sensors implanted in the body, for instance, we can use a waterproof polymer film to completely encapsulate the sensor or apply a waterproof polymer coating to the outermost layer to minimize the effects of corrosion and dissolution, thereby increasing their lifetime. In the case of self-powered sensors used for motion monitoring, we should focus on the construction of chemical bonds between the molecular chains to improve the mechanical strength of the hydrogel so that it can be applied to the long-term detection of reciprocating mechanical motion. If the hydrogel sensor is used in air or at low temperature for a long time, it is necessary to pay attention to moisture-retention and freezing behavior to improve performance stability and service life.

Self-powered hydrogel sensors are playing an increasingly important role in the fields of smart interaction, wearable devices, health care, and environmental monitoring. Many of these diverse

applications share some common requirements for durability, minimal impact on their surroundings (and sometimes biodegradability) and the need to collect multiple physical and chemical signals. These requirements could be answered using the adaptably hydrogel chemistry. Self-powering could also open new opportunities in the design and fabrication of autonomous sensor arrays. This will require a parallel effort to develop the tools required to collect, integrate and interpret complex signal patterns. These tools have to be non-invasive and fast. To do this, research in sensors will have to be integrated with recent advances in areas as diverse as electronics, wireless communication, computer science and artificial intelligence. When it comes to sensor development, the preparation of high-performance materials, the optimization of device structures, and the multi-function, integration and miniaturization of end products are still the main research challenges. Addressing these issues requires collaboration among scholars in different research fields such as biology, chemistry, physics, and materials science to advance the development of a family of devices that could have a very large impact in the transition to a healthier, net-zero society.

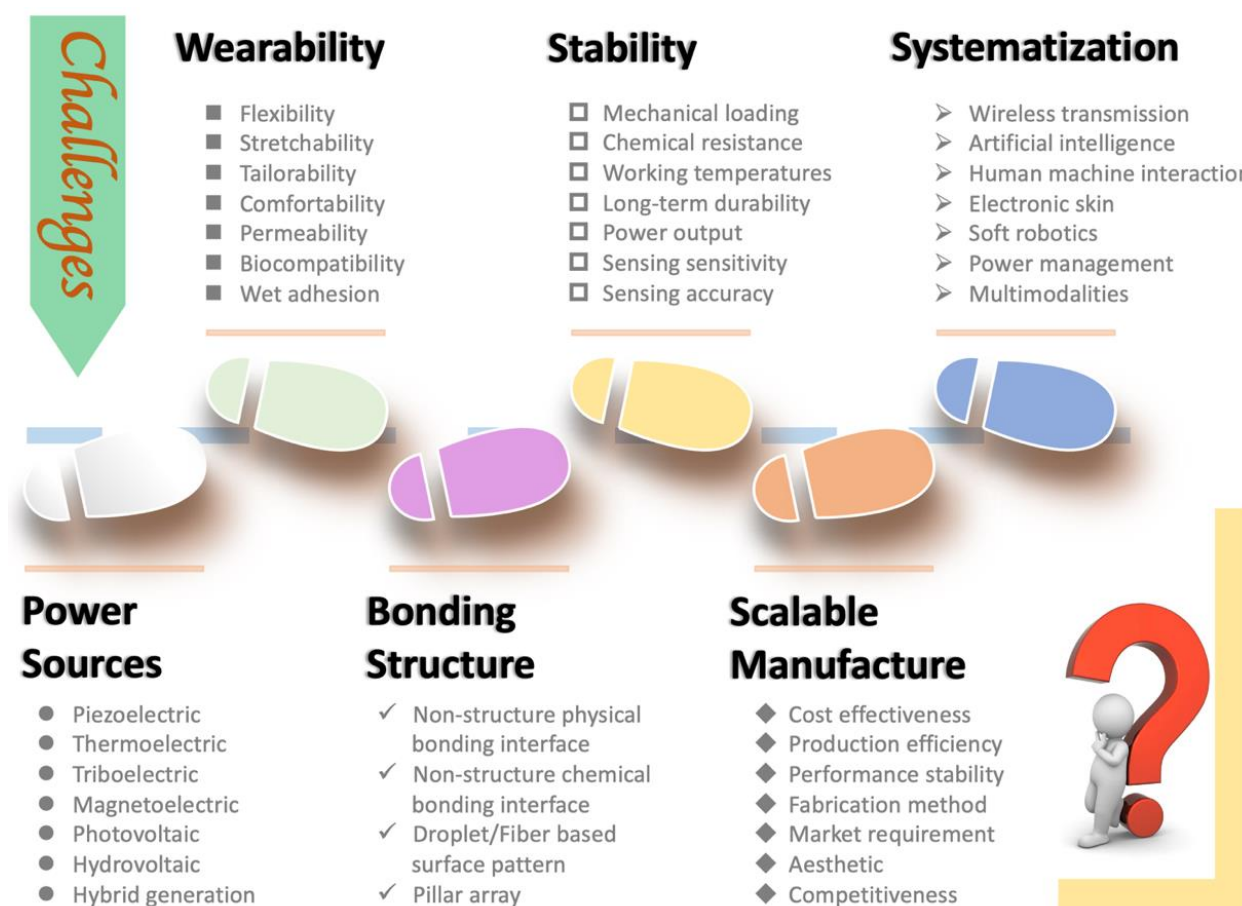


Figure 6. Roadmap for the development of self-powered hydrogel sensors.

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Author contributions

Ming Li conceived and designed the project. Ming Li and Qingwen Guan wrote the main content of the paper, they contribute equally to this work. Chang Li assisted the writing and revision of the manuscript. Eduardo Saiz revised the content of article and provided useful suggestions. All authors discussed and commented on the manuscript.

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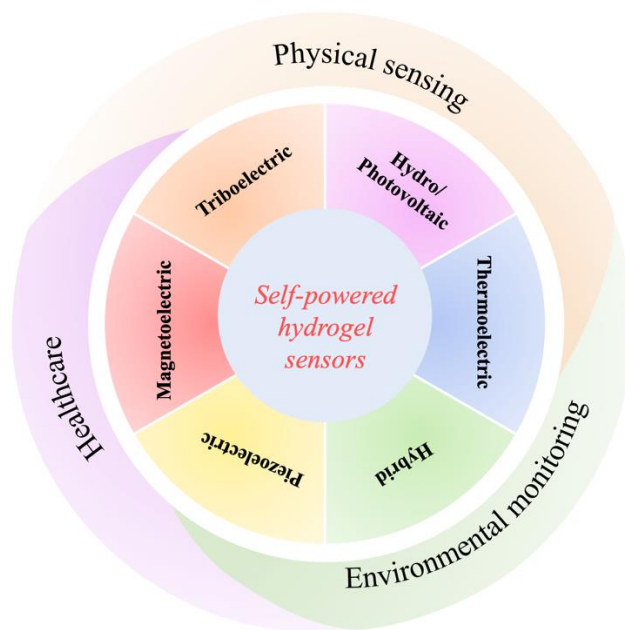


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