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REVIEW

Development of conductive hydrogels: from design mechanisms to frontier applications

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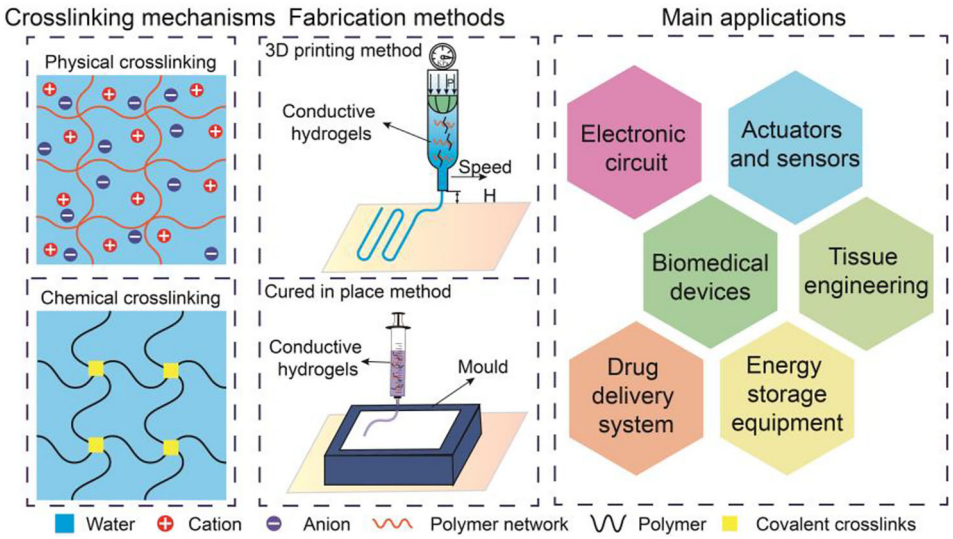
Abstract

Owing to their excellent mechanical flexibility, electrical conductivity, and biocompatibility, conductive hydrogels (CHs) are widely used in the fields of energy and power, and biomedical technology. To arrive at a better understanding of the design methods and development trends of CHs, this paper summarizes and analyzes related research published in recent years. First, we describe the properties and characteristics of CHs. Using Scopus, the world's largest abstract and citation database, we conducted a quantitative analysis of the related literature from the past 15 years and summarized development trends in the field of CHs. Second, we describe the types of CH network crosslinking and basic functional design methods and summarize the three-dimensional (3D) structure-forming methods and conductive performance tests of CHs. In addition, we introduce applications of CHs in the fields of energy and power, biomedical technology, and others. Lastly, we discuss several problems in current CH research and introduce some prospects for the future development of CHs.

Graphic abstract



Keywords Conductive hydrogels · Crosslinking mechanism · Design methods · 3D structure-forming methods · Conductive hydrogel applications

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Introduction

Hydrogels composed of water and hydrophilic polymers are a type of porous-structured polymer material with high bioaffinity. They exhibit desirable properties such as stretchability, self-healing, and transparency [1] and thus have a wide range of applications in biomedical and optical devices. Some applications include contact lenses and artificial tissues. Hydrogels can be classified as natural or synthetic hydrogels according to their source materials. Natural hydrogels are generally directly derived from nature (such as gelatin and chitosan) and have high biocompatibility. However, there are significant challenges in the practical application of natural hydrogels. For example, many natural hydrogels suffer from low mechanical strength, an uneven distribution of crosslink density, and a lack of adhesion—undesirable hydrogel properties. In contrast, synthetic hydrogels (such as polyvinyl alcohol and polyacrylamide) can provide sufficient mechanical strength and other properties. However, they can face problems such as insufficient biodegradability and biocompatibility problems which limit their application in the biomedical field. Therefore, traditional hydrogels all have shortcomings and challenges to overcome [2].

Based on this, research has been carried out to modify the physical and chemical characteristics of traditional hydrogels to develop smart hydrogels. These smart hydrogels can respond to different physicochemical stimuli, such as electric fields, magnetic fields, temperature, and light [3]. Among these hydrogels, electro-responsive hydrogels have significant potential in the fields of actuators, sensors, soft electronic devices, and tissue engineering—owing to their good electrical conductivity, transparency, and biocompatibility [4–9]. Electro-responsive hydrogels are generally referred to as conductive hydrogels (CHs). They include hydrogel systems that respond to small electric-field changes and consequent changes in properties (shrinkage, swelling, or bending). CHs generally consist of a crosslinked hydrophilic polymer matrix and conductive fillers (metal nanoparticles, carbon-based materials, and conductive polymers) [10], which are mainly constructed using two types of methods: (1) the addition of hydrophilic crosslinking agents to the dispersion system of the conductive polymer to cause it to be crosslinked into the CHs; (2) the in situ generation of conductive polymers in hydrogels to make the hydrogels conductive [11, 12]. CHs can be made to have widely tunable physicochemical properties by combining various conductive components with different kinds of polymer matrices [13–15].

In 2013, Keplinger et al. [16] first published an application study on transparent ionic CHs, making possible the application of CHs. Thereafter, research on CHs has rapidly generated high-impact results. The bibliometric analysis data in Fig. 1 are based on Scopus database retrieval statistics, and the data include papers published online. Figure 1a shows the trend of development of the research field of hydrogels and CHs. It arguably indicates that the field of CH research is significantly expanding. Prior to 2007, most research papers about hydrogels and CHs were sporadic, exploratory papers. Since 2007, the number of papers on these two topics has grown exponentially. After 2017, the growth rate of papers on hydrogel research has increased steadily every year, whereas the number of papers on CH research has increased more rapidly (reflected by the change in the slope of the broken line in the data graph). Figure 1b shows the publication of conference papers and high-level journal papers on CH research in the past 15 years. The number of conference papers has remained stable, whereas the number of high-level journal papers has grown rapidly. For high-level journal papers with an impact factor (IF) > 10, the number of publications in 2021 is nearly twice that of 2020. Figure 1c shows the proportion of high-level journal papers on CH research with an IF > 10 in the past 15 years. Figures 1b and 1c show that the field of CH research has attracted worldwide attention and has been among the current frontiers of scientific research.

However, there exist few comprehensive introductions regarding CHs. Thus, this review aims to provide a detailed overview of the different types of CHs proposed in the scientific literature and to analyze and summarize their basic principles to provide new ideas for the development of CHs. First, this review introduces the types and characteristics of CH-network crosslinks and basic design ideas. Second, it provides a summary of the two main three-dimensional (3D) structure-forming methods based on CHs, supplemented by testing methods for their electrical conductivity. At the same time, based on the performance characteristics of CHs, this review summarizes their applications in the fields of energy and power, instrument science, electronic science, and biomedical technology. Lastly, this review discusses current development problems and future research trends of CHs.

Typical crosslinking types and functional design methods of conductive hydrogels

Typical crosslinking types of conductive hydrogels

The formation of CHs mainly relies on physical or chemical interactions to connect crosslink sites on the polymer network, namely, physical and chemical crosslinking [17]. Physical crosslinking and chemical crosslinking of CHs are distinguished mainly by their different properties, such as their reversible and mechanical characteristics (as shown in Table 1). The type of crosslinking is a key factor in analyzing the structure of CHs and is the basis for causing them to exhibit different properties. Moreover, rational molecular

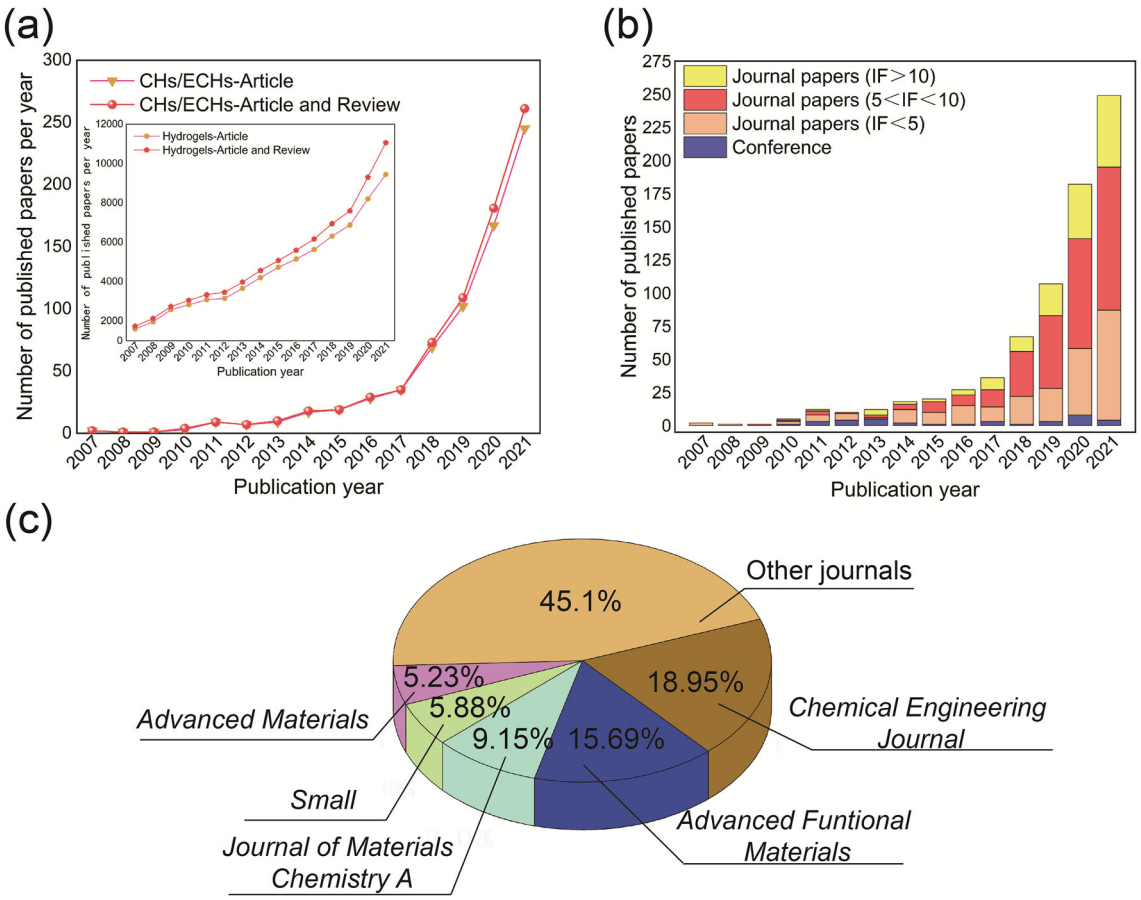

Fig. 1 Bibliometric analysis of the CH research field in the past 15 years based on the Scopus database (data as of February 26, 2022). **a** Search statistics based on the Scopus database. The search used the following keywords in the title, abstract, and keywords: "hydrogels" or "hydrogel," "conductive hydrogels," or "electroconductive hydrogels" or "conductive hydrogel" or "electroconductive hydrogel"; document types: "article" and "review"—for search results from 2007 to 2021 for statistics of the relevant published papers. **b** Keywords: "conductive hydrogels" or "electroconductive hydrogels" or "conductive hydrogel" or "electroconductive hydrogel," literature publication source: "journal" and "conference", literature types: "article" and "review," and statistics of the search results. Relevant papers published from 2007 to 2021 were divided into conference papers, journal papers with an IF<5, journal papers with an IF between 5 and 10, and journal papers with an IF>10. **c** Based on the literature data in (**b**), a statistical analysis was performed on the number and proportion of relevant literature in all journals with an IF>10

network design can allow CHs to satisfy different performance requirements [18]. The following sections introduce physical and chemical crosslinking and briefly introduce the hybrid crosslinking derived from them.

Physical crosslinking

Physical crosslinking is a type of reversible (non-permanent), weak crosslinking that is commonly used in the preparation of hydrogels. It results in the formation of a hydrogel network (shown in Fig. 2a) through the physical bonding of different polymer chains, including hydrogen bonding [19, 27], hydrophilic interactions [28, 29], hydrophobic interactions [30–32], and ionic bonding [33–35]. Examples of materials that exhibit reversibility include some natural polymer materials such as K-type carrageenan, which show a relatively stable gel state at room temperature. However, when the temperature reaches a certain threshold, it changes from a gel state to a sol state. Some synthetic polymer materials also exhibit this reversibility. For example, polyvinyl alcohol (PVA) can form hydrogels with stable properties at 60 °C after being processed by freezing and thawing.

Hydrogen bonding Hydrogen bonding is a common reversible physical crosslinking method [20]. The higher the proportion of hydrogen bonds, the stronger is the resulting hydrogel. Currently, researchers have carried out much pioneering exploration on hydrogels based on hydrogen-bond crosslinking [36]. For example, Dai et al. [37], inspired by double- and triple-hydrogen bonds in double-stranded deoxyribonucleic acid (DNA), produced an increasing boost of hydrogen-bonding interactions using polymer chains with

Table 1 Comparisons of advantages and disadvantages of physical crosslinking and chemical crosslinking technology

Type of crosslinking	Characteristics	Advantages	Disadvantages	References
Physical crosslinking	Non-permanent (reversible)	(1) Simpler to prepare (2) No need to use toxic crosslinking agents (3) The mechanical properties and mechanical strength of hydrogels can be improved to a certain extent through method improvement	(1) The resulting hydrogels are generally structurally unstable and have poor mechanical properties (2) There may be uneven swelling distribution (3) Limited to physical crosslinking between a limited number of components	[2, 19–21]
Chemical crosslinking	Permanent (irreversibility)	(1) The resulting hydrogel is generally stable in structure and has good mechanical properties (2) Not limited by the number of components (3) It has substrate specificity, keeps effective reactions continuous, and avoids ineffective reactions (4) "Click chemistry" has high efficiency, high stability, high specificity, and strong control, which conforms to the requirements of chemical synthesis for molecular diversity	(1) Toxic crosslinking agents are required in the chemical crosslinking process (2) Chemical crosslinking is not all controllable, and the degree of controllability is limited (3) There may be uneven swelling distribution	[2, 21–24]
Hybrid crosslinking		Combines the advantages of physical and chemical crosslinking and avoids their limitations		[25, 26]

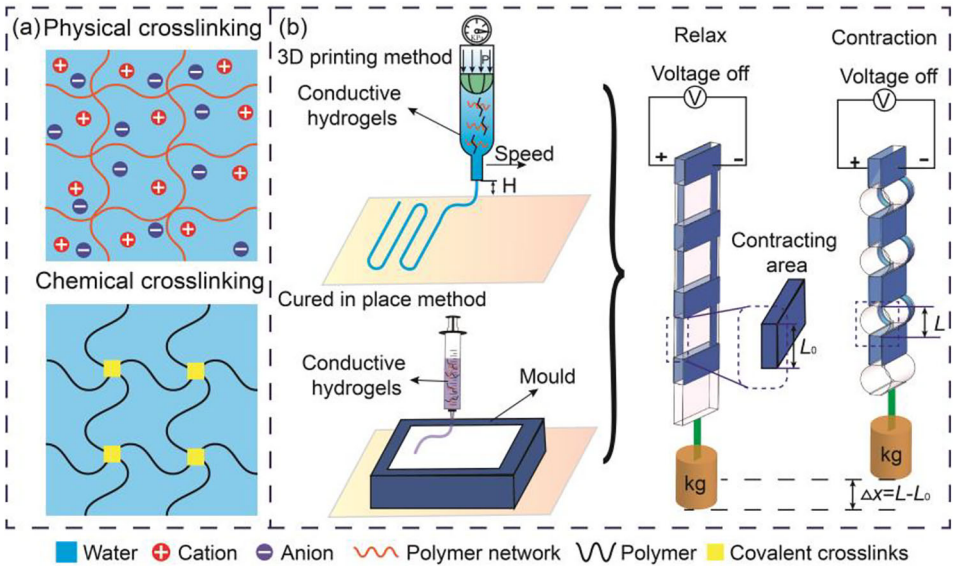

Fig. 2 **a** Types of crosslinking in hydrogel networks; **b** 3D structure-forming methods of CHs and application mechanisms of the actuators

an array of hydrogen-bonding sites, which increased mechanical strength. In 2021, Guo et al. [38] used this method of hydrogen bonding to develop PDA (polydopamine)-PAM (poly(acrylic acid))/Mg^{2+} hydrogel with self-healing and with strong adhesive properties.

Ionic interaction Ionic interaction is also a common physical crosslinking method. It is achieved by the interaction of ionizable polymers with cations [39]. Currently, a cation's valence state determines the degree of crosslinking, which provides a controllable mechanism for the crosslinking

process of hydrogels. For example, the mechanical properties of hydrogels formed by adding $CaCl_2$ to alginate are controlled by crosslink density, and desired mechanical properties can be achieved by controlling the proportion of Ca^{2+} components [22]. Poly(3,4-ethylenedioxythiophene):poly (styrene sulfonate) (PEDOT:PSS) nanofibers phase will be changed into physical crosslinking hydrogels under the action of ions and becomes a kind of composite hydrogel with an interpenetrating network having a conductivity as high as ~1.74 S/m [40].

Hydrophobic interaction Another physical crosslinking method is hydrophobic interaction. The formed hydrogels can disperse any external force through micelles in the structure [41]. This characteristic originates from the reversible binding and dissociation activities of the hydrophobic groups within the hydrogels. Crystallization is also a form of physical crosslinking where the mechanical properties of hydrogels obtained by crystallization can usually be altered by changing the concentration of the water phase, the number of freeze–thaw cycles, and the molecular weight.

Physical crosslinking is simpler in mechanism than chemical crosslinking and is reversible. Although it can improve the mechanical properties and mechanical strength of hydrogels to a certain extent, there are related deficiencies in mechanical strength and life.

Chemical crosslinking

Chemical crosslinking hydrogels, also known as "true hydrogels" (as shown in Fig. 2a), are irreversible (permanent) polymers with a 3D network structure formed by chemical crosslinking. They generally have better mechanical properties than physical crosslinking hydrogels [22]. Chemical crosslinking mainly includes photopolymerization [42–44], enzymatic crosslinking [45–47], and thermal polymerization [48, 49].

Photopolymerization crosslinking Among these chemical crosslinking methods, photopolymerization crosslinking is commonly used and can be carried out under mild conditions. Photopolymerization crosslinking generally requires cooperation between photosensitizers and activating light, and photons can be used to selectively activate specific regions for crosslinking. For example, polymers containing methacrylate groups are often highly sensitive to ultraviolet (UV) radiation and are often used as UV photosensitizers for photopolymerization crosslinking [50, 51]. So, methacrylic acid and hyaluronic acid have become a common photopolymerized crosslinking hydrogel [52, 53].

Enzymatic crosslinking In contrast to photopolymerization crosslinking, which has experimental environmental requirements, the enzymatic crosslinking method can be carried out under normal conditions (at room temperature). This method is stable, non-toxic, and substrate-specific [54]. Enzymatic crosslinking forms hydrogels by forming strong covalent bonds. Therefore, the process is generally shorter. For example, polyethylene glycol/hyaluronic acid hydrogels are generated under the action of transglutaminase and can be used for biomedical cell and tissue regeneration [55].

Click chemistry "Click chemistry" is another chemical crosslinking method—a new technology proposed by Sharpless in 2001. The high efficiency, stability, and controllability of Click chemistry has revolutionized the field of chemical synthesis. The core concept of Click chemistry involves the use of carbon-heteroatom bonding reactions to rapidly achieve molecular diversity, generally by the interaction of azide and alkyne to form covalent bonds. The reaction process is not affected by pH and can be carried out in water at room temperature, even in living cells. The method of Click chemistry complies with the requirements of chemical synthesis on molecular diversity and corresponds to different polymer conjugation methods.

Other chemical crosslinking methods Researchers have also developed other chemical crosslinking methods besides the methods mentioned above. For example, Parada et al. [56] covalently grafted elastic polymer networks in hydrogels to elastomer chains via the benzophenone crosslinker to achieve robust bonding between the hydrogels and elastomer layers. Liu et al. [23] mixed a silane coupling agent into the precursors of the hydrogels and hydrophobic elastomer network and added the coupling agent to the polymer chain without condensation as the network formed. The coupling agent gradually condenses after the fabrication step to form chemical covalent bonds within the network, which also enables the independent bonding and fabrication of CHs.

The process of chemical crosslinking requires the use of more crosslinking agents compared to physical crosslinking. However, most crosslinking agents are hazardous [57]. Both physical crosslinking and chemical crosslinking have their own advantages, disadvantages, and limitations [21]. Hybrid crosslinking could be considered a solution. It is a type of composite crosslinking that combines the advantages of physical and chemical crosslinking and avoids their disadvantages [25, 26]. Therefore, the biomedical application of CHs synthesized by hybrid crosslinking has attracted considerable attention.

Functional design methods of conductive hydrogels

CHs can be divided into electron-conductive hydrogels (E-CHs) and ion-conductive hydrogels (I-CHs), according to their conductive components [1]. Different conductive

Table 2 Comparisons of characteristics and applications of E-CHs and I-CHs

Type of CHs	Common characteristics	Contrast characteristics	Applicable fields	References
E-CHs	Highly stretchable, conductive, biocompatible, transparent	Better electronic conductivity, better biocompatibility	Bioengineering field (biosensors, tissue engineering, drug delivery devices)	[58–63]
I-CHs		Ionic conductivity, capable of generating ionic gradients	Energy storage and conversion devices (drives, nanogenerators); transparency devices (displays, touch panels)	[64–67]

components or doping methods affect the conductive properties of CHs. CH characteristics and application areas are shown in Table 2. In addition to basic conductive properties, CHs perspectively possess other properties, such as high stretchability, frost resistance, stimuli responsiveness, and self-healing. These properties can be obtained through reasonable design strategies. The following sections specifically introduce the basic functional design methods of CHs based on different conductive components.

Electron-conductive hydrogels (E-CHs)

There are three main types of conductive components in E-CHs: metal nanoparticles (Au, Ag, etc.) [68–70], carbon-based materials (carbon grease, carbon nanoparticles/carbon nanotubes, etc.) [71–73], and conductive polymers (polypyrrole, PEDOT:PSS, etc.) [74–76]. In regard to the preparation process of E-CHs, the simplest method is to mix conductive components into the hydrogel matrix to form E-CHs. However, the E-CHs formed by this method have low electrical conductivity, poor mechanical properties, and no practical application value. Researchers have found that the introduction of specific intermolecular interactions (covalent bonds and non-covalent bonds) between the conductive components and the polymer matrix can stabilize and cause the E-CHs to be more viable [77–81].

Metal nanomaterials are commonly used conductive components in E-CHs and have the characteristics of high electrical conductivity and high specific surface energy. For example, Devaki et al. [82] combined in situ polymerization of acrylic acid and in situ reduction of Ag^+ to develop kinds of E-CH with uniform networks (shown in Fig. 3a). Later, the researchers integrated the photoreduction of Ag^+ and the photopolymerization of polyethylene glycol diacrylate in one system and quickly generated complex 3D structures with good electrical properties (up to $\approx 2.2 \times 10^7$ S/m) based on 3D-printing technology [83]. Besides silver, gold is also a common importable material. In 2016, Baei et al. [69] introduced uniformly dispersed, gold nanoparticles into heat-sensitive CHs based on chitosan. In the same year, Navaei et al. [70] embedded gold nanorods in gelatin-based CHs, and the work of both groups was successfully applied to cardiac tissue engineering. The introduction of metal nanomaterials has little effect on the mechanical properties, and so these E-CHs are widely used in various stress-responsive sensors.

Compared to metal nanomaterials, carbon-based materials generally build 3D-conductive networks in hydrogel matrices by establishing an electron transport pathway of π-conjugated structures. E-CHs made from carbon-based materials have a high specific surface area and abundant surface functions. This can improve mechanical properties [71]. For example, Han et al. [84] utilized polydopamine-modified carbon nanotubes to prepare CHs by the in situ polymerization of acrylic acid and acrylamide in water or glycerol solutions. These carbon nanotubes exhibit resistance to freezing and heat and can be used as persistent strain sensors under extreme conditions (as shown in Fig. 3b). Subsequently, Liang et al. [72, 73] proposed adding polydopamine-coated, carbon nanotube dispersions to a solution of gelatin-grafted dopamine and chitosan to generate CHs through dopamine oxidative coupling. Their fabricated E-CHs could promote skin regeneration with electrical conductivity and an antibacterial effect and free radical scavenging capabilities (as shown in Fig. 3c). In addition, the CHs obtained by dispersing carbon nanotubes in alginate hydrogels can promote the growth of bacterial colonies and collect the electrons generated by the cells, something which can be used to monitor the electrical activity of microorganisms [85]. Furthermore, the incorporation of carbon nanotubes and laponite nanoclay into poly (N-isopropyl acrylamide) (PNIPAM) hydrogels yields photothermally responsive CHs with high stretchability, self-healing, and adhesion, which can be used in wearable body sensors [86, 87].

In addition to the aforementioned two materials, the addition of conductive polymers can also complete the transfer of electrons. The functional design methods of E-CHs based on conductive polymers generally include the following forms: (1) polymer monomers and conjugated molecules are simultaneously dissolved in water and polymerized separately; (2) conductive polymer hydrogels (such as polyaniline) are

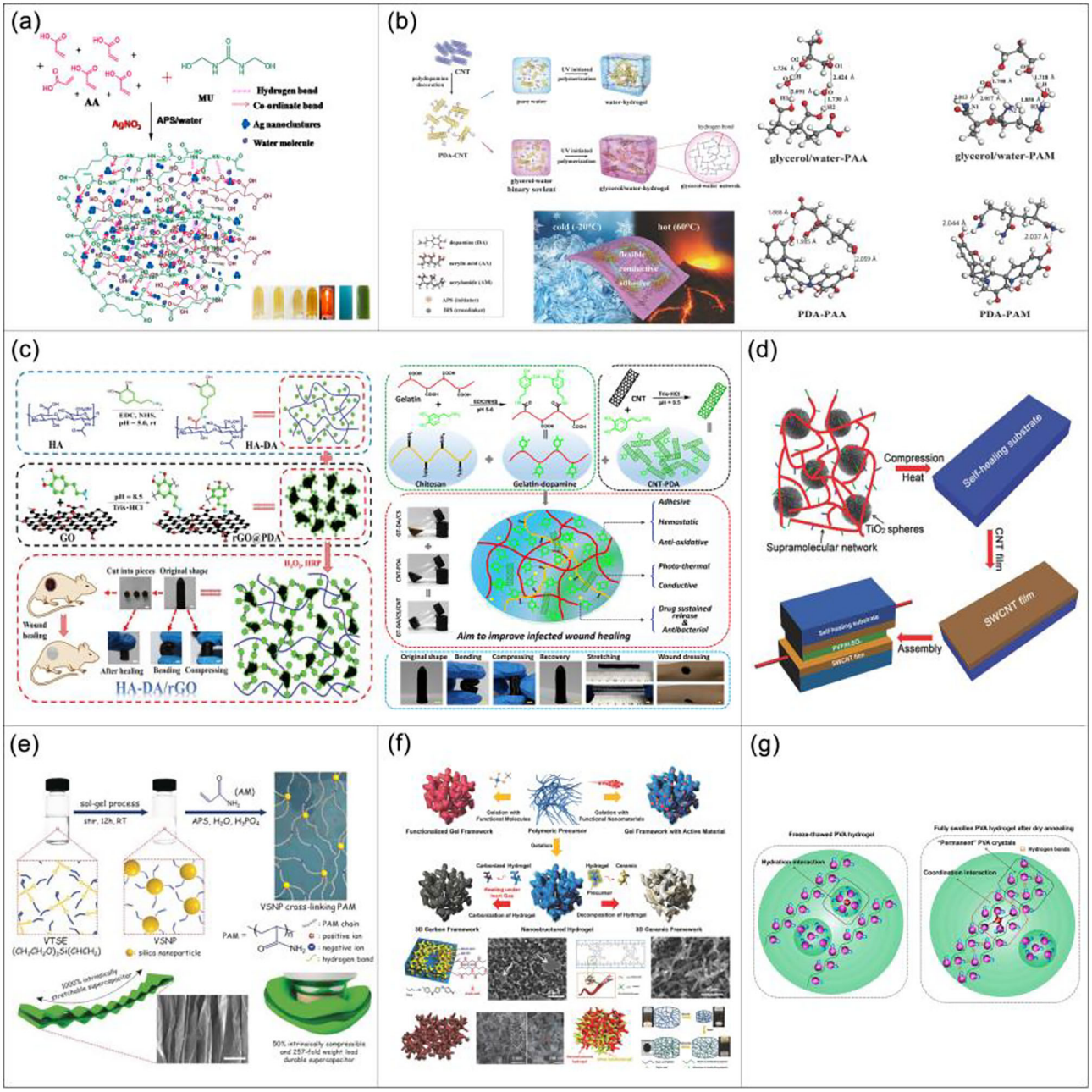

Fig. 3 Examples of functional design methods for CHs: **a** mechanism of the formation of silver nanoparticles (reproduced from [82], Copyright 2014, with permission from Elsevier); **b** CHs with long-lasting moisture and extreme temperature tolerance based on glycerol-water binary solvent (reproduced from [84], Copyright 2017, with permission from WILEY–VCH Verlag GmbH & Co. KGaA, Weinheim); **c** schematic representation of GT (gelatin)-DA (dopamine)/CS(chitosan)/CNTs(carbon nanotubes) hydrogel preparation; synthesis scheme of GT-DA polymer; scheme of HA (hyaluronic acid)-DA/rGO(reduced graphene oxide) hydrogel and the original, bending, compressing, self-healing representation, and the application in wound healing (the left subfigure is reproduced from [73], Copyright 2019, with permission from WILEY–VCH Verlag GmbH & Co. KGaA, Weinheim; the right subfigure is reproduced from [72], Copyright 2019, with permission from Elsevier); **d** the design and manufacturing process flow of a flexible, electrically and mechanically self-healing supercapacitor (reproduced from [91], Copyright 2014, with permission from WILEY–VCH Verlag GmbH & Co. KGaA, Weinheim); **e** schematic of the intrinsically 1000% stretchable supercapacitor (reproduced from [92], Copyright 2017, with permission from WILEY–VCH Verlag GmbH & Co. KGaA, Weinheim); **f** schematic illustration of general functionalization strategies of nanostructured functional hydrogels (reproduced from [93], Copyright 2018, with permission from WILEY–VCH Verlag GmbH & Co. KGaA, Weinheim); **g** design principle for the ionic hydrogel of PVA and NaOH with synergistic coordination and hydration interactions (reproduced from [94], Copyright 2021, with permission from the authors)

prepared by crosslinking conductive polymer chains with phytic acid; (3) conductive polymer hydrogels form based on self-crosslinking conductive polymer networks. Because polyaniline has good biocompatibility, most E-CHs involving polyaniline are used for tissue engineering or metabolic monitoring [76]. In addition, E-CHs based on polypyrrole can be prepared by adjusting the solubility of pyrrole to produce CHs with excellent properties [62]. The hydrogel dPEDOT-CA-PDA-PAM can also be integrated with flexible microcircuits to develop a bioadhesive ultrasoft brain-machine interface (BMI) [63]. PEDOT has excellent electrical conductivity and electrochemical stability in its oxidation state and its complex with PSS is water-soluble. PEDOT:PSS can be directly doped into the hydrogel matrix, and PEDOT can be functionalized with carboxyl and pendant groups with double bonds to prepare the expected E-CHs [88]. Metal nanoparticles and conductive polymers can also be mixed together into one system to achieve desirable electrical and mechanical properties.

Ion-conductive hydrogels (I-CHs)

The porous structure of hydrogel polymer networks can trap large amounts of water while allowing the water molecules to move freely. The high mobility of ions in water provides the foundation for the functional design of ion-conductive hydrogels (I-CHs) [89]. Currently, materials that can provide free ions for hydrogels are divided mainly into three categories: acids (HCl, H_2SO_4, etc.), metal salts (NaCl, LiCl, etc.), and ionic liquids (1-ethyl-3-methylimidazolium chloride, etc.). I-CHs have different characteristics in comparison with E-CHs, including high transparency, high mobility, and others. Some specially designed I-CHs also have strong water retention properties [90] or ultra-low temperature antifreeze properties [84], and their extremely strong durability and environmental adaptability expand their application range.

I-CHs are suitable for the fabrication of energy storage and energy conversion devices (such as batteries, drives, etc.) and have become the backbone of the development of a new generation of electronic technologies. In recent years, a new type of energy storage device called the "supercapacitor" has attracted much attention. Supercapacitors function like traditional batteries but have higher efficiency and longer life spans. The general approach to fabricating supercapacitors based on I-CHs is to dissolve an acid into a polymer hydrogel to render the hydrogel's protons conductive. For example, the introduction of H_2SO_4 into polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP) hydrogels can produce high-performance solid electrolytes and self-healing supercapacitors [91, 95] (as shown in Fig. 3d). Additionally, supercapacitors with stretch-compression properties can be prepared by adding H_3PO_4 to silica nanoparticle crosslinking PAM hydrogels [92] (as shown in Fig. 3e). I-CHs are also well suited for use as electrolytes in batteries. Compared with liquid electrolytes commonly used in batteries, electrolytes based on I-CHs do not leak, are non-volatile and non-combustible, and are safer, more stable and more efficient [93, 96] (as shown in Fig. 3f).

Thermoelectric energy technology is also an area in which I-CHs can be applied. In 2021, Chen et al. [94] announced research progress pertaining to a new ionic hydrogel thermoelectric material. This material achieved a large negative thermoelectric potential (up to −37.61 mV/K) through cooperative coordination and hydration. Chen et al. dispersed NaOH into freeze-thawed PVA hydrogels with a dry-annealing process at 100 °C followed by a full-swelling process. This treatment process enabled a stronger coordination structure between PVA and Na^+ in order for it to exist stably in the hydrogel, resulting in a large negative thermoelectric potential (as shown in Fig. 3g). This new ionic hydrogel thermoelectric material is flexible, cost-effective, and has promising applications in the design of ionic thermoelectric materials with high thermoelectric performance, low-grade thermal energy harvesting, and temperature sensing.

3D structure-forming methods and electrical conductivity test methods of CHs

3D structure-forming methods of CHs

After understanding crosslinking mechanisms and functional design methods, the 3D structure-forming process of CHs is directly related to their performance and applications. Appropriate methods, effective designs, and precise manipulation are prerequisites for developing hydrogels with high performance and improvement of processing. Currently, 3D structure-forming methods of CHs are mainly divided into the in situ cured-in-place mold method [97–99] and the 3D-printing method [100–105] (the characteristics and differences of the two methods are shown in Table 3). The cured–in–place mold method is more efficient for simple and regularly shaped hydrogels, but it is more difficult to process for irregular shapes, and the material-utilization rate is low. In contrast, the 3D-printing method removes a reliance on molds and therefore, hydrogels with more complex shapes can be made [106]. There are additional special auxiliary 3D structure-forming methods that can assist in the fabrication of hydrogels with better properties, which will be discussed in a later section.

Cured–in–place mold method

The in situ cured-in-place mold method uses a prefabricated mold which holds the hydrogel solution for curing combines a processing technology, such as laser cutting, for further

Table 3 Comparisons of characteristics between cured-in-place mold method and 3D-printing method

Characteristics	Cured–in–place mold method	3D-printing method	References
Whether a mold is required	Yes	No	[97–105]
Whether post-processing is required	Yes	No	
Cost of materials and equipment	Lower	Higher	
Difficulty	Ordinary	Higher	
Speed	Ordinary	Higher	
Precision	Ordinary	Higher	
The complexity of the shapes that can be prepared	Lower	Higher	
Mode	Fixed	Can be designed according to actual needs	

improvements [107]. The in situ cured-in-place mold method is widely used by researchers because of its simple operation and because of environmental conditions. Keplinger et al. [16] poured a PAM hydrogel solution containing a photoinitiator into a pre-prepared sheet-like glass mold and covered it with a glass plate. They then cured the hydrogels at a wavelength of 254 nm for 20 min with the help of a UV-light crosslinker. After the solution was cured and formed, they were machined into circular and heart-shaped driver electrodes designs using a laser cutting machine (as shown in Fig. 4a). To explore the difference in water retention of different I-CHs, Bai et al. [90] prepared four kinds of PAM hydrogel samples containing different ions (NaCl, LiCl, KaC, and $MgCl_2$) using a self-made glass mold for the experiments (as shown in Fig. 4b). The entire cured-in-place process was accomplished by gelling in a chamber at a constant temperature chamber of 50 °C for 2–5 h.

Using the same material as Keplinger, Acome et al. [108] used a 365 nm wavelength UV light to cure for 1 h and became the first research team to successfully produce a practical, hydraulically amplified, self-healing electrostatic (HASEL) actuator. Depending on the application, they cured the in situ hydrogel solution in one of two different ways. The first was to cast a 200-μm-thick PAM-LiCl CHs electrode onto a 25.4-μm-thick Kapton film and then perform laser cutting to obtain a circular electrode after curing. The second was a flexible electrode that was cast onto the prepared polydimethylsiloxane (PDMS) mold substrate and directly cured into the desired shape by means of UV light with a wavelength of 365 nm (as shown in Fig. 4c). Based on this, Kellaris et al. [97] fabricated a higher-performance actuator "Peano-HASEL" by casting the PAM-LiCl CHs solution onto a 160-μm-thick PDMS mold substrate, followed by post-shape processing after the same curing process as that of Acome et al. (as shown in Fig. 4d). The Peano-HASEL actuator has a controllable linear contraction (up to 10%), a strain rate of 900%, a drive frequency of 50 Hz, and the ability to lift objects over 200 times its own weight. The CHs electrode preparation method used by Mitchell et al. [109] is similar to the 3D structure-forming method of the CHs electrode driven by Peano-HASEL (as shown in Fig. 4e).

3D-printing method

At the beginning of hydrogel research, in situ cured-in-place mold method was the only method for 3D structure forming. With the development of 3D-printing technology, complex hydrogel preparation has become easier [107]. 3D printing enabled the configuration of hydrogel inks according to the designed shape and structure by setting the corresponding speed and other additional parameters [110, 111]. Thus, 3D printing enabled rapid prototyping and mass customization and is an ideal method for processing CHs [112–114].

Ying et al. [115] first mixed methacrylic anhydride gelatin (GelMA) with polyethylene oxide (PEO) to prepare bioinks. By changing the concentration of PEO during ink preparation, hydrogels with different pore sizes could be obtained and the desired porous structure of the hydrogels could be processed by 3D printing (as shown in Fig. 5a). In contrast to conventional 3D-printing techniques, Truby et al. [116] used embedded 3D-printing technology to print I-CH soft sensors into soft robotic fingers. This method is dominated by multiple conductive features, which can be simultaneously tactile, thermal, and proprioceptive (as shown in Fig. 5b). This embedded 3D-printing technology ensures the seamless integration of multiple ionic conductors and fluid properties, resulting in ideal biosensing and actuation capabilities. This method can be used to fabricate soft somatosensitive actuators and has strong application prospects in building soft robots and haptic devices that require multimodal perception. General 3D printing has the limitation of a fixed printing order. However, in 2019, Yang et al. [100] published a method to print the overall structure of hydrogels and elastomers in arbitrary order. The hydrogels and elastomers printed by this method have extremely high fracture energies (10,000 J/m^2 and 6000 J/m^2, respectively) and adhesion energies (5000 J/m^2). During the printing process, the monomer units are connected, forming a polymer network, and the two hydrogel networks and the elastomer are crosslinked by covalent bonds to form an overall structure (as shown in Fig. 5c). To directly apply 3D-printed hydrogels to the biomedical

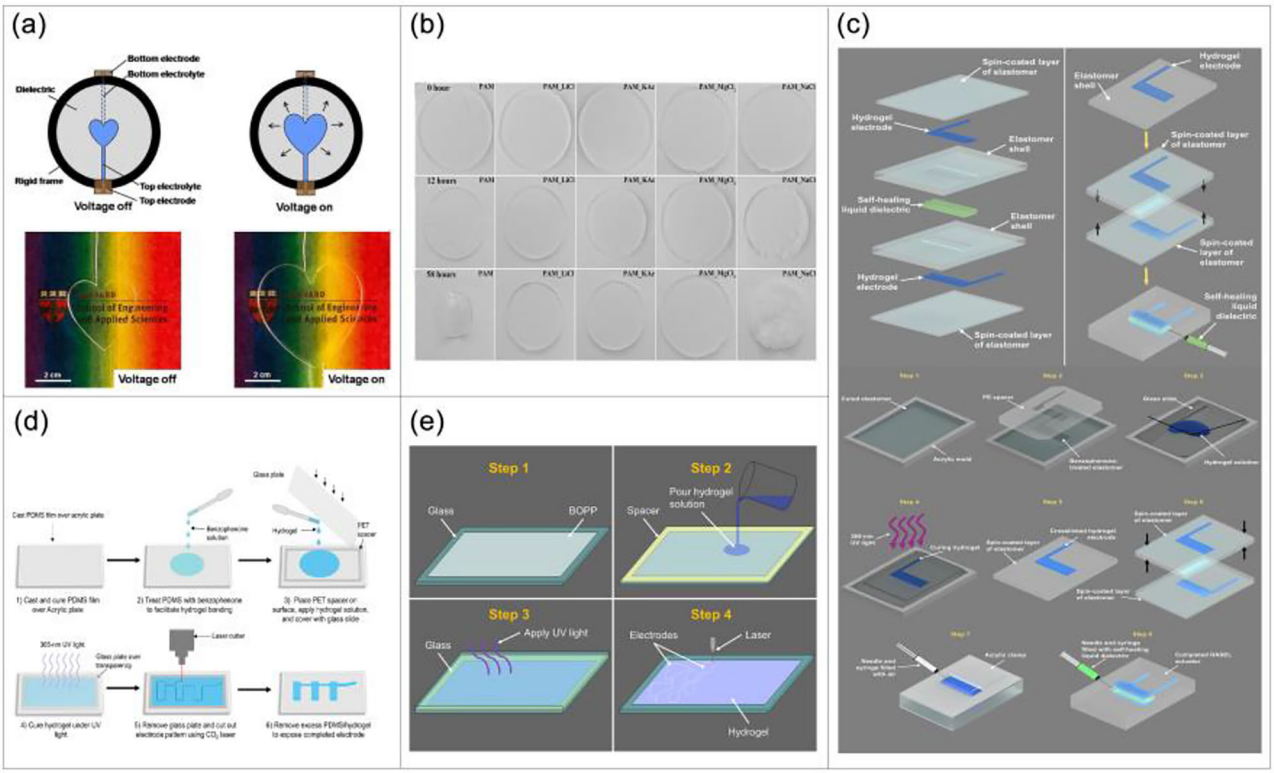

Fig. 4 Examples of the cured–in–place mold method: **a** a heart-shaped PAM-LiCl I-CHs electrode driver (reproduced from [16], Copyright 2013, with permission from American Association for the Advancement of Science); **b** PAM hydrogels were prepared with NaCl, LiCl, KaC, and $MgCl_2$ as electrolytes (reproduced from [90], Copyright 2014, with permission from AIP Publishing); **c** components and manufacturing steps of a single-unit HASEL driver, using an elastomer mold to directly in situ cure into the desired shape of conductive hydrogel electrode (reproduced from [108], Copyright 2018, with permission from the authors); **d** fabrication process for Peano-HASEL actuators with hydrogel electrodes (reproduced from [97], Copyright 2018, with permission from the authors); **e** fabrication process of hydrogel electrodes (reproduced from [109], Copyright 2019, with permission from the authors)

field, Shao et al. [117] proposed a biocompatible 3D-printing method. They used gelatin as a sacrificial complement to print a complex GelMA hydrogel structure with a human-like vascularized network (as shown in Fig. 5d). Based on this, Shao et al. [118] continued to conduct in-depth research and developed a new GelMA-based bioink. This new bioink is suitable for printing porous GelMA hydrogel structures where the microgelatin gel is embedded as a sacrificial component (as shown in Fig. 5e). The porous GelMA hydrogel structure printed with this embedded sacrificial microgelatin gel is more suitable for cell spreading.

In 2021, much was achieved in the 3D-printing technology of CHs. Xue et al. [120] designed and fabricated single-layer composite CHs with bulk capacitive junctions, which can be used to construct "SHARK" (single-layer hydrogel artificial skin) with multiple sensing modes and fast self-healing properties. The 3D-printing system is very suitable for the manufacturing of complex sensor chips with printing accuracies down to 200 microns. Zhu et al. [40] combined PEDOT:PSS materials and PAM hydrogel matrices with photocuring technology and fabricated electroluminescent devices and capacitive sensors using a self-designed 3D-printing system based on digital light processing (as shown in Fig. 5f). Combined with photocurable materials, this 3D-printing system can fabricate a variety of sophisticated and complex structures with high resolution (~70 μm). Dong et al. [119] proposed a fabrication method for constructing nanoporous, superhydrophobic structures using a projection photocuring 3D printing method. Although the main object of this study is not hydrogels at present, the proposed 3D-printing strategy can be extended to the processing and molding of hydrogels (as shown in Fig. 5g).

In general, the 3D-printing method and the in situ curing method have their own characteristics in terms of cost, technical difficulty, and applicable fields, and should be selected according to what is required.

Special auxiliary 3D structure-forming methods

Beyond the two basic 3D structure-forming methods, certain properties of CHs can be significantly improved by adding special auxiliary processing during the processing,

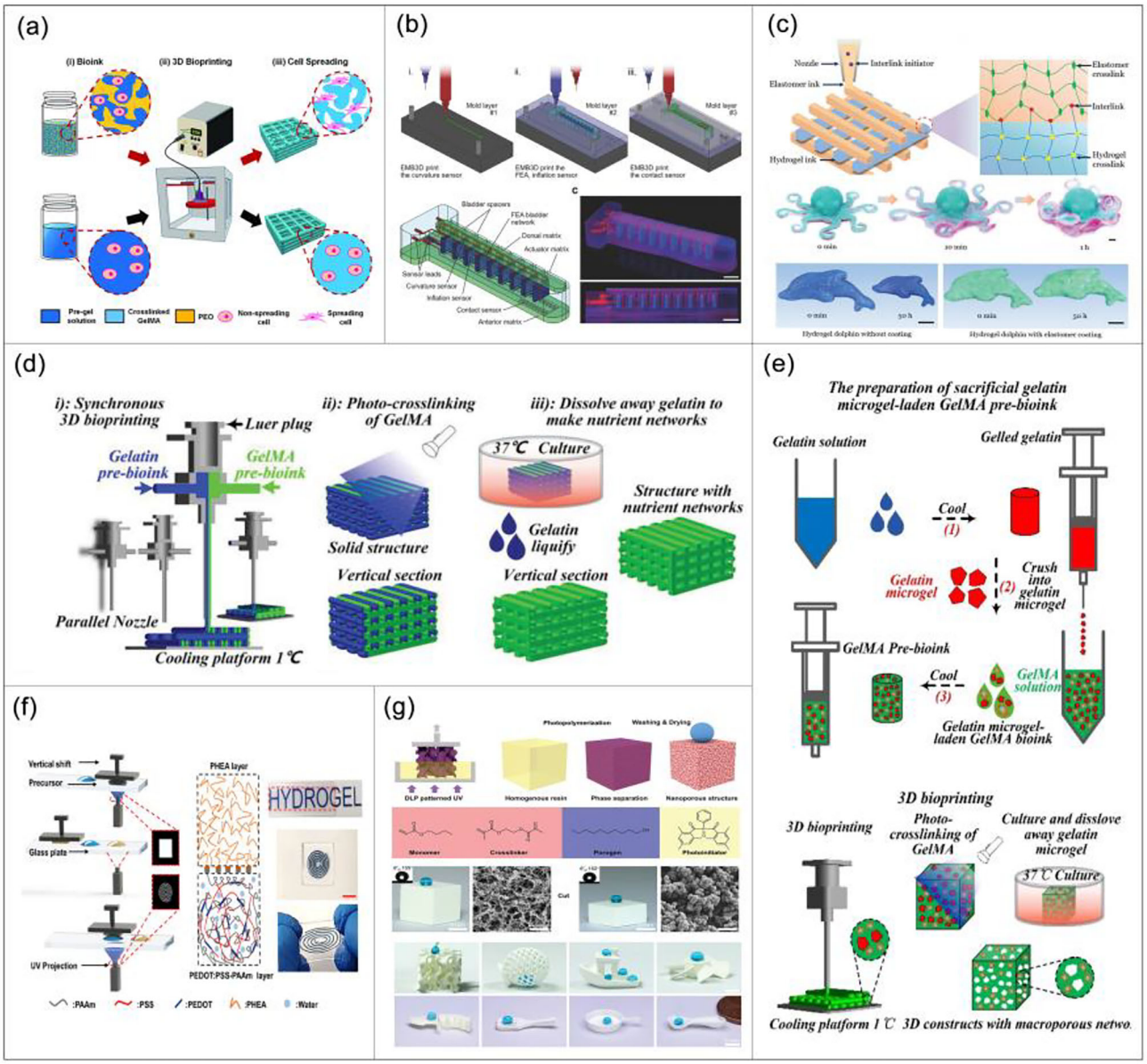

Fig. 5 Examples of 3D-printing methods: **a** 3D printing of porous GelMA hydrogel structures with a sacrificial PEO component (reproduced from [115], Copyright 2018, with permission from WILEY–VCH Verlag GmbH & Co. KgaA, Weinheim); **b** fabrication of a soft somatosensitive actuator innervated with multiple soft sensors (reproduced from [116], Copyright 2018, with permission from WILEY–VCH Verlag GmbH & Co. KgaA, Weinheim); **c** an approach to print integrated structures of a hydrogel and an elastomer, in arbitrary sequence and with strong adhesion (reproduced from [100], Copyright 2019, with permission from WILEY–VCH Verlag GmbH & Co. KgaA, Weinheim); **d** 3D-printed complex GelMA hydrogel structures with vascularized networks via multimaterial and sacrificial gelatin inks (reproduced from [117], Copyright 2019, with permission from WILEY–VCH Verlag GmbH & Co. KgaA, Weinheim); **e** 3D printing of porous GelMA hydrogel structures with sacrificial gelatin microgels (reproduced from [118], Copyright 2020, with permission from Zhejiang University Press); **f** schematic representation of the conductive hydrogel–elastomer manufacturing process and demonstrations (reproduced from [40], Copyright 2021, with permission from American Chemical Society); **g** 3D printing of superhydrophobic objects with a bulk nanostructure (reproduced from [119], Copyright 2021, with permission from the authors)

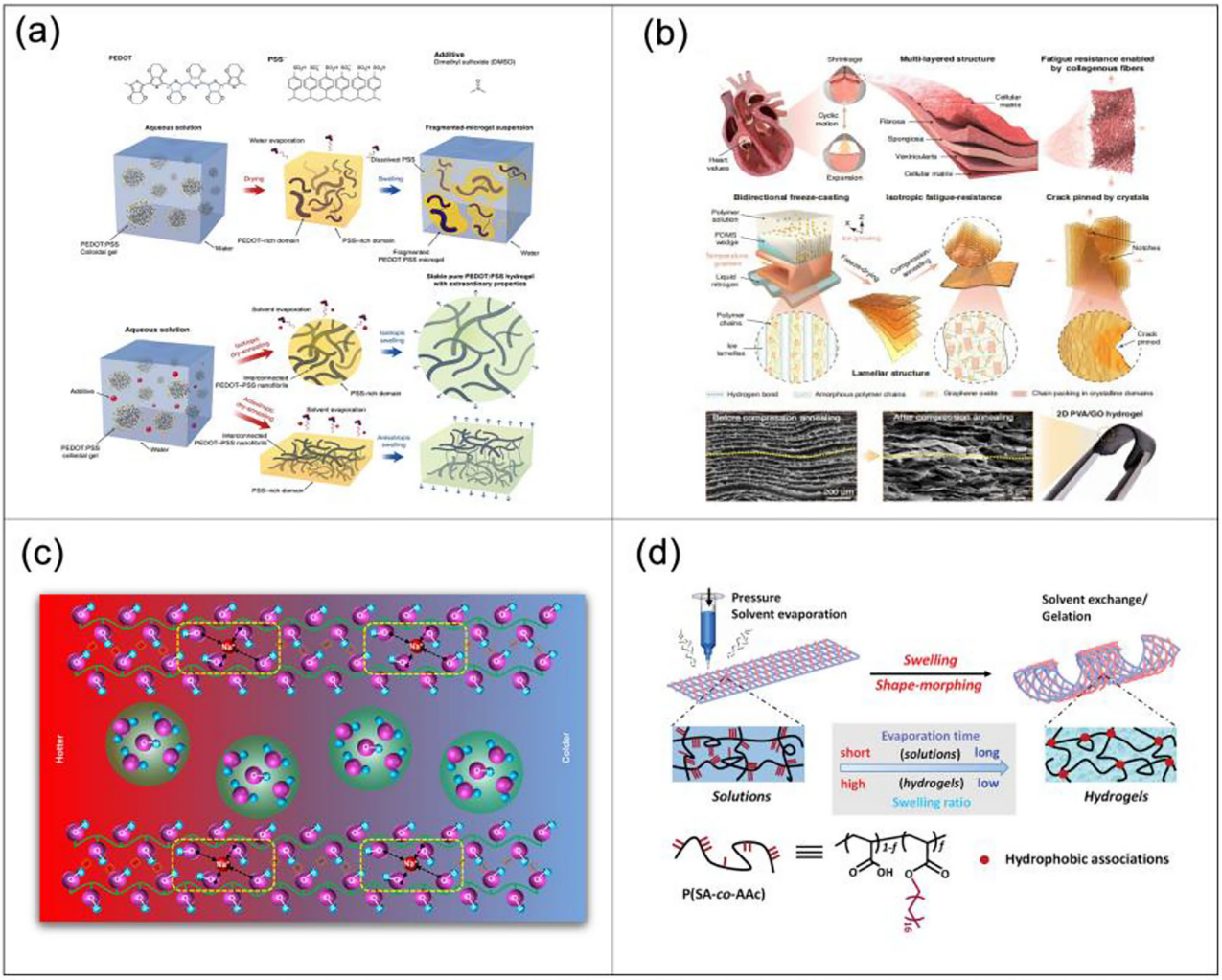

Fig. 6 Examples of special preparation methods: **a** schematic illustration of pure PEDOT:PSS hydrogel preparation (reproduced from [88], Copyright 2019, with permission from the authors); **b** fabrication of hydrogels with 2D lamellar structures (reproduced from [122], Copyright 2022, with permission from Wiley–VCH GmbH); **c** schematic figure of interactions in the as-fabricated ionic thermoelectric materials of NaOH-PVA hydrogels under the temperature gradient (reproduced from [94], Copyright 2021, with permission from the authors); **d** schematic of the solvent-cast printing of ethanol solution of poly(stearyl acrylate-co-acrylic acid) and the shape morphing of printed gel constructs after swelling in water (reproduced from [123], Copyright 2021, with permission from Wiley–VCH GmbH)

which can expand their application range. For example, Naficy et al. [121] developed a PEDOT:PSS-based CH with strong compatibility and extremely high electrical conductivity (up to 4.3 S/cm). Following this, Lu et al. [88] first added the volatile additive dimethylsulfoxide into the PEDOT:PSS solution. They promoted the recrystallization of PEDOT nanofibers and the chain rearrangement of PEDOT:PSS by increasing the dry-annealing process. Finally, a high-performance PEDOT:PSS CH with an interconnected network of nanofibers was prepared via a hydration reaction (as shown in Fig. 6a). The conductivity of PEDOT:PSS CH in deionized water was greatly improved and reached 40 S/cm.

Inspired by the unique structure of heart valves, Liang et al. [122] designed a PVA/GO (graphene oxide) anti-fatigue hydrogel with a two-dimensional (2D) oriented isotropy (as shown in Fig. 6b). During the preparation process, they first formed neatly aligned layers of microstructures or nanostructures through a bidirectional freeze-casting process, followed by compression and annealing. The prepared hydrogels exhibit excellent anti-fatigue properties in any direction of the 2D plane (the fatigue threshold exceeds 1500 J/m^2) and can be used to manufacture the power and actuator components of soft robots. Chen et al. [94] also incorporated the dry-annealing process and developed an I-CH thermoelectric material that achieves a sizable negative thermoelectric potential through cooperative coordination and hydration (as shown in Fig. 6c). They first dispersed NaOH into freeze-thawed PVA hydrogels, followed by a dry-annealing process

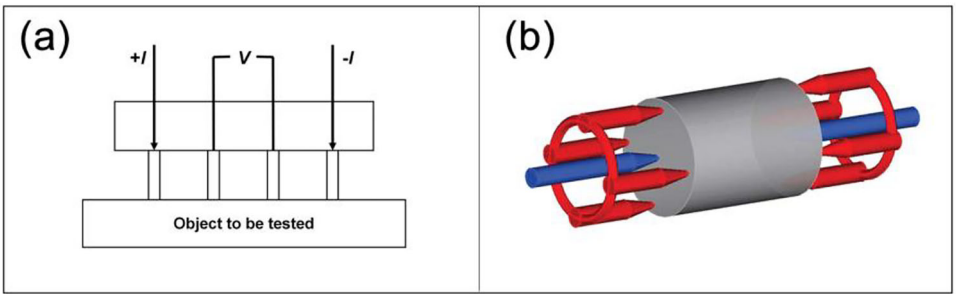

Fig. 7 Schematic of the 4-point probe measurement method: **a** schematic of a 4-point probe configuration; **b** schematic of an improved device of 4PPM—the central electrodes (marked with blue) are the sense electrodes to measure sample voltage; the red electrodes are the force electrodes (multiple on each side) to apply the stimuli in a uniform manner; the gray cylindrical shape corresponds to the actual sample being measured (reproduced from [126], Copyright 2018, with permission from Oxford University Press)

at 100 °C. After continuous experimentation and improvements, they determined the optimal annealing time (90 min) and NaOH concentration (0.9 mM) conditions. According to these optimized conditions, CH thermoelectric materials with high thermoelectric potential in the range of −19.69 to 37.61 mV/K can be prepared. Simultaneously, they confirmed that the dry-annealing process at a high temperature (100 °C) can promote the stable coordination structure in I-CH thermoelectric materials. Overall, this CH thermoelectric material is flexible, transparent, of low-cost, and is cost-effective, and can be used in wearable energy storage devices and temperature sensors.

Excluding special processes, the overall combination of CHs and elastomers presents a new way to utilize the performance advantages of both. To facilitate the integration of the CHs and the elastomer during the application process, it is also a feasible 3D structure-forming method to directly use the elastomer as a mold for metal-like casting [123, 124]. For example, Guo et al. [123] developed a facile method for constructing deformable hydrogel structures based on solvent casting-assisted printing (as shown in Fig. 6d). Using the expansion mismatch caused by solvent evaporation, they obtained different deformable hydrogel structures by controlling the pattern of the printing process. This casting method extends from metal fabrication to the preparation of hydrogels and has been a success in both fields.

Electrical conductivity test methods of conductive hydrogels

Electrical conductivity (generally referred to as conductivity σ) is one of the most important quality indicators of CHs, and electrical conductivity is usually closely related to the processing and molding process. Therefore, this section aims to describe electrical conductivity test methods of CHs. As early as 1997, Pissis and Kyritsis [125] published a paper on the study of the electrical conductivity of hydrogels. With the development of hydrogel research, research on their electrical conductivity and testing methods has been increasing. There are many factors that affect the conductive properties of CHs, and the types of conductive particles, particle concentration, shape, and environmental humidity all have different degrees of influence. This section mainly introduces a commonly used electrical conductivity test method—the 4-point probe measurement method (4PPM). This method can measure the general volume or thin film samples, and different samples correspond to different expressions [126]. For the calculation of the sample conductivity σ (Eq. (1)), three parameters can be obtained from the measurements to obtain the unknown parameter conductivity σ. In the formula, R is the resistance of the sample, l is the thickness of the sample, and S is the cross-sectional area of the sample.

$$\sigma = \rho^{-1} = l/(RS). \tag{1}$$

The 4PPM device designed based on the above method is shown in Fig. 7a. The device has a pressurization device inside it where the probes at both ends measure the current and the middle two probes measure the voltage drop. The 4PPM device calculates the resistance value R according to the measurement data, and the electrical conductivity of the hydrogels can be calculated according to the conductivity calculation formula—Eq. (1). Although this device can measure electrical conductivity, the range that can be measured by a typical 4PPM device is limited. Chandra et al. [127] improved the design of a 4PPM device using a RepRap 3D printer to facilitate large-area, 4-point probe measurements. Compared with two other proprietary test systems, their research results achieved excellent performance at the same level of accuracy with 30% lower costs. In addition to the measurement range, measurement accuracy is also an area that can be optimized. Kaklamani et al. [126] optimally designed a 4PPM device (as shown in Fig. 7b). They provided more accurate sample voltage sensing by spatially separating the force electrode and the sense electrode to further reduce the impact of electrode

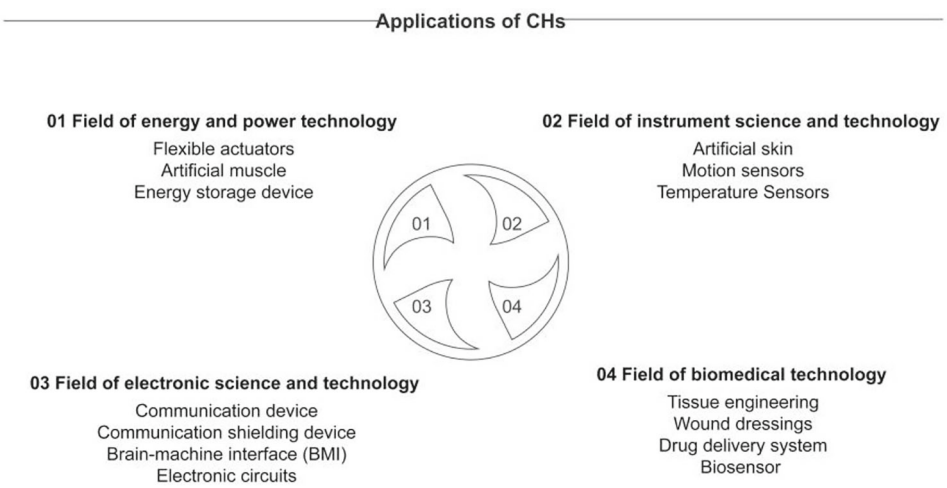

Fig. 8 Applications of CHs in various research fields

resistance on the measurement results, and they maximized the accuracy of the measurement results.

Applications of CHs

As a branch of hydrogels, CHs not only have better electrical conductivity, but also have advantages in flexibility, high ductility, transparency, and biocompatibility. Based on these unique advantages, CHs can be made into one-dimensional (1D) fibers with excellent performance. Inspired by spider silk, Zhao et al. [128] developed a simple spinning method to prepare CH fibers with ordered polymer chain alignment. This conductive fiber has excellent stretchability, electrical conductivity, and frost resistance. It will enable the design of next-generation textile-based stretchable electronic devices. CHs based on 1D fibers have many applications in 2D thin films and 3D bulk forms in many fields. This is precisely because researchers continue to overcome various limitations, and CHs have gradually begun to gain attention in many important fields. The following sections introduce applications of CHs in the following four fields: energy and power, instrument science, electronic science, and biomedical technology—based on current research (as shown in Fig. 8).

Field of energy and power technology

Actuating technology is a core application in the field of energy and power technology. In contrast to other commonly used electrode materials such as graphite and metal, CHs have unique advantages which include high ductility, excellent electrical conductivity, and transparency. Therefore, CHs are often used in flexible actuator electrodes with high requirements because they can minimize contact with the actuator while maximizing actuating performance.

The use of CHs as the core component in soft actuating technology has achieved strong application results in many fields [64]. Underwater actuating technology is one aspect of CH applications. For example, inspired by the shape of manta rays, a soft electroactive structure made of PAM hydrogel as the electrode material drove electronic fish to move in water at a speed of 6.4 cm/s (0.69 of body length) (as shown in Fig. 9a) [99]. The electronic fish is driven by the PAM hydrogel electrode, and the surrounding water is a bridge between positive and negative electrodes. Changing the amplitude and frequency of the voltage can change its swimming speed. With the transparent properties of the hydrogel material, it appears almost invisible in the water and can navigate undetected. In 2021, Liang et al. [122] designed a jellyfish-like underwater robot using PVA/GO anti-fatigue CH film as the robot's head to provide a driving force (as shown in Fig. 9b). After a high-strength experiment of 1,094,400 stretching, and shrinking cycles, the head of the robot only produced slight plastic deformation, showing ideal fatigue resistance in practical applications.

Artificial muscle is also a potential application of CH actuating technology. In 2018, Acome et al. [108] announced a new soft actuator named "HASEL" (hydraulically amplified self-healing electrostatic) as shown in Fig. 9c. HASEL actuators have human-muscle-like performance and are self-healing with the support of internal transformer oil. This research provides a valuable reference for the development of soft robotics and artificial-muscle technology. In the same year, Kellaris et al. [97] improved the original HASEL actuator. They also proposed a soft electro-hydraulic actuator "Peano-HASEL" with reference to the linearly contracting Peano fluid actuators studied by Niiyama et al. [129] and Sanan et al. [130] (shown in Fig. 9d). The Peano-HASEL actuator still uses PAM hydrogel as the electrode material while combining the advantages of fluidic and electrostatic actuators. It utilizes electrostatic and hydraulic principles to

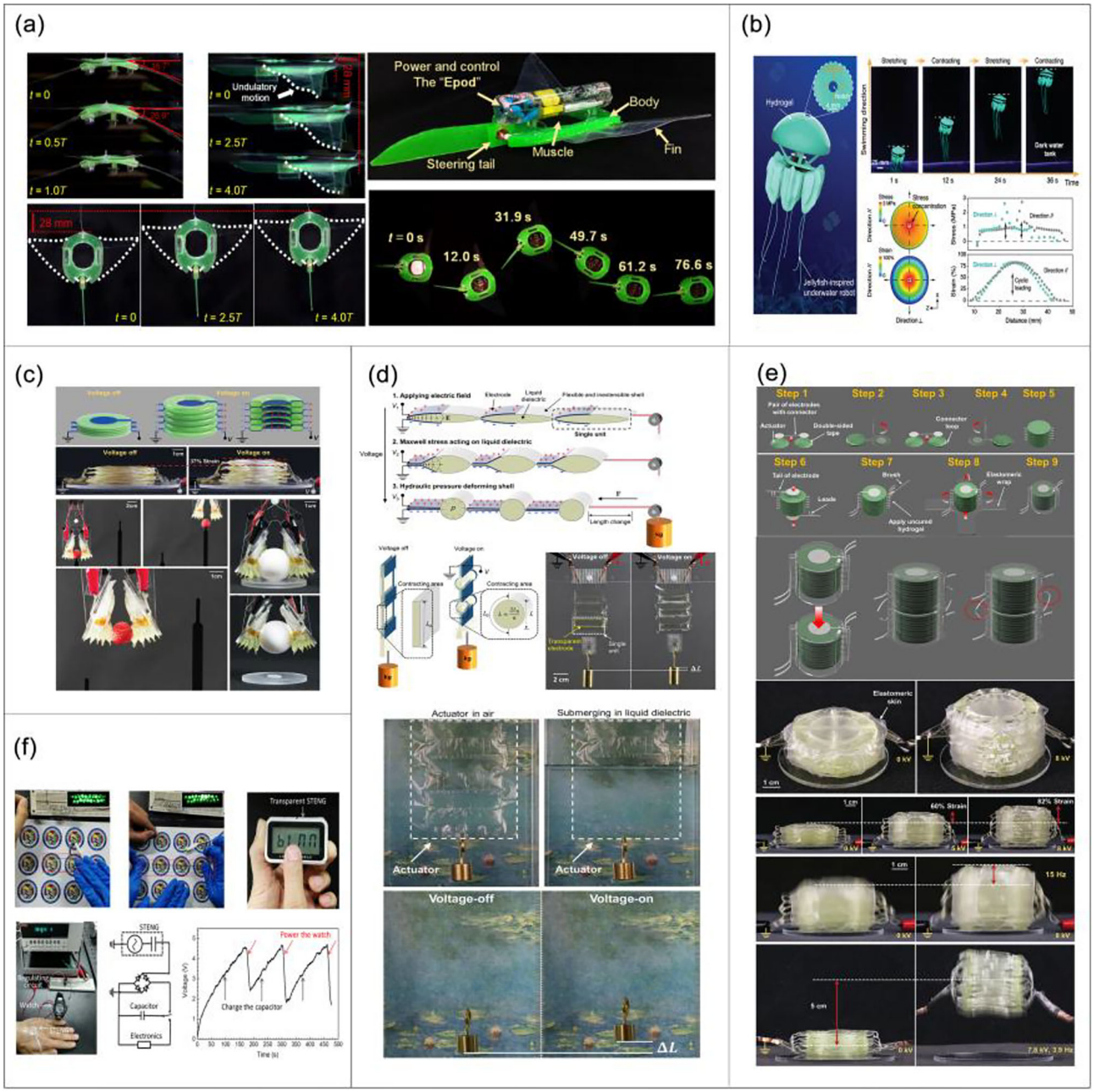

Fig. 9 Applications of CHs in the field of energy and power technology: **a** live snapshots of swimming untethered electronic fish with wired power (reproduced from [99], Copyright 2017, with permission from the authors); **b** application of 2D PVA/GO hydrogel as the loadbearing components for a jellyfish-inspired underwater robot (reproduced from [136], Copyright 2017, with permission from the authors); **c** stacks of donut HASEL actuators operating as linear actuators and soft grippers (reproduced from [108], Copyright 2018, with permission from the authors); **d** basic components of invisible Peano-HASEL actuators and principles of operation (reproduced from [97], Copyright 2018, with permission from the authors); **e** stacking process to create modular units of quadrant donut HASELs and a demonstration of the performance of stacked quadrant-donut HASELs (reproduced from [109], Copyright 2019, with permission from the authors); **f** biomechanical energy harvesting by STENG and an image of 20 green LEDs lighted by VHB-STENG (reproduced from [122], Copyright 2022, with permission from Wiley–VCH GmbH)

linearly contract (up to 10% linear contraction) in a muscle-like manner when a voltage is applied. Ideally, it can lift objects over 200 times its weight and is extremely responsive. In addition, Peano-HASEL possesses transparency and the ability to self-perceive in its deformed state. Therefore, the Peano-HASEL actuators have broad application prospects in the fields of biomedicine, industrial automation, and autonomous robotic devices. Later in 2019, Mitchell et al. [109] designed an artificial muscle with comprehensive actuating performance (with three basic actuating modes of expansion, contraction, and rotation) based on the HASEL actuator (as shown in Fig. 9e). It achieved more than 100% linear strain with a specific power greater than 150 W/kg and generated approximately 20% strain at frequencies above 100 Hz. The team also developed a modular design-and-manufacture approach that can be used to expand the application of this new type of software-efficient actuator.

Energy storage technology is also one of the typical applications of CHs. Achieving mechanical ductility and certain self-healing properties in energy storage technology has always been a technical problem [10]. The excellent mechanical ductility and self-healing ability of CHs make them an ideal material for energy storage devices. Soft supercapacitors based on CHs have been widely studied and practically applied due to their excellent performance. In 2016, Li et al. [131] developed a high-performance polyaniline–polyvinyl alcohol hydrogel (PPH) for flexible solid-state supercapacitors (SSC). PPH shows remarkable tensile strength (5.3 MPa) and electrochemical capacitance (928 F/g). The flexible SSC based on PPH provides a large capacitance (306 mF/cm^2 and 153 F/g) and a high energy density of 13.6 W·h/kg—superior to other flexible supercapacitors. Then, in 2017, Li et al. achieved another breakthrough [132]. The new PPH-5 shows remarkable tensile strength (16.3 MPa), large elongation at break (407%), and higher electrochemical capacitance (1053 F/g). The flexible SSC based on PPH-5 provided a larger capacitance (420 mF/cm^2 and 210 F/g) and higher energy density (18.7 W·h/kg). Furthermore, PEDOT—PVA hydrogel had been used to develop a flexible SSC [133, 134]. This SSC can operate at a high voltage of 1.4 V, which provides a high-energy density up to 24 W·h/kg (with a power density of over 200 W/kg). Also, it had a high number of rechargeable cycles. In addition, a highly stretchable and conductive polypyrrole hydrogel with a unique biphase microstructure (loose phase and dense phase) can be used to fabricate novel SSCs [135]. The dense phase enables the PPy-hydrogel high tensile strength (2 MPa) and strong conductivity (0.8 S/cm). Without using any substrate, the SSC made of this polypyrrole hydrogel provides an areal capacitance of 950 mF/cm^2 at a current density of 1.6 mA/cm^2, exceeding most reported SSCs.

In addition to energy storage devices, CHs can be used in special "electric generators". Pu et al. [136] developed a soft and skin-like triboelectric nanogenerator (STENG) using PAM-LiCl CHs as the electrode material, which achieved a biomechanical energy harvesting effect (as shown in Fig. 9f). STENG can output alternative electrical energy (instantaneous peak power density of up to 35 mW/m^2), which provides a new concept for the functional design of multifunctional power supplies and wearable electronic products. On this basis, Zhou et al. [137] designed a new type of CH ion diode to collect low-frequency mechanical energy and convert it into a high output current (13.5 μA/cm^2), which overcomes the shortcoming of the performance of STENG in a low-frequency range (such as that of human motion of less than 1 Hz). The parallel structure of 5 units after further stacking can produce an output current of 64.3 μA/cm^2 and a power density of 0.48 μW/cm^2. Moreover, the STENG, based on I-CHs, further realizes important functions such as those of self-healing and anti-pollution, laying a foundation for applications in human–computer interaction, health monitoring, and other fields [138].

Field of instrument science and technology

The characteristics of strong electrical conductivity, high stretchability, tunable responsiveness, and biocompatibility make CHs a popular material for soft sensor applications. Sensors made of CHs are not limited by the shape and application range of traditional sensors, such as artificial skin, motion sensors, and temperature sensors [139–141].

"Artificial skin" is generally defined as a stretchable film with capacitive pressure sensors that can perform sensing functions similar to human skin. Materials such as graphene sheets and gold nanomesh can use electrons for signal transmission and possess electrical conductivity and ductility, but do not have the biocompatibility and optical transparency of real skin. Various CH-based skin-like devices have been used in wearable sensors, soft robotic sensing, energy harvesting, and in human monitoring [3]. For example, Sun et al. [98] exploited the high stretchability, transparency, and biocompatibility of CHs to develop a transparent "ionic skin" (as shown in Fig. 10a). They sandwiched an elastomer layer with two metal electrodes between two PAM-LiCl CH layers, and the entire sensor was encapsulated by the outer two layers of VHB. It was sensitive enough to detect the touch of a finger, fulfilling the basic function of a "skin". Sarwar et al. [142] also developed a CH-based sensor array. This sensor array can sense multiple gentle finger touches even when bent and stretched, whereas STENG [136], with a skin-like shape, can monitor the applied pressure using its own generated current and voltage signals without the need for an external power source. STENG has an ultra-high stretching ability and high transparency (adjustable according to actual needs) and can sense pressure as low as 1.3 kPa (sensitivity is 0.013 kPa^{-1}). The team fabricated a 3×3 array

Fig. 10 Applications of CHs in the field of instrument science and technology: **a** stretchable transparent ionic skin (reproduced from [98], Copyright 2014, with permission from WILEY–VCH Verlag GmbH & Co. KgaA, Weinheim); **b** the design of transparent and superstretchable STENG and tactile sensing by the STENG (reproduced from [136], Copyright 2017, with permission from the authors); **c** to realize the monitoring of various external stimuli, strain, temperature, and humidity sensors were integrated into one substrate to fabricate multifunctional e-skins (reproduced from [86], Copyright 2021, with permission from the authors); **d** images of a 12×12-inch PNIPAM-AEMAA device (reproduced from [143], Copyright 2019, with permission from Elsevier); **e** the operating principle of a thermoresponsive colorimetric sensor and colorimetric visualization of the thermoresponsive smart colorimetric patch (reproduced from [144], Copyright 2018, with permission from the authors)

of skin-like pressure sensors using STENG materials and conducted related experiments and applications (as shown in Fig. 10b). Self-healing is another technical issue that needs to be addressed for "artificial skin" based on CHs. Lin et al. [86] developed a multifunctional electronic skin with dual-layer autonomous self-healing ability (as shown in Fig. 10c). They first mixed various carbon materials such as carbon black, carbon nanotubes, and graphite with a self-healing binder slurry. Various functional units (such as electrodes, strain sensors) were then fabricated on one surface, and these devices simultaneously exhibited excellent performance and self-healing capabilities. By spraying water on the damaged part, both the functional layer and the flexible substrate could heal themselves in about 10 min. Various devices can maintain the sensitivity and stability of the original devices even under large deformation after self-healing. At the same time, this soft, self-healing electronic skin can be connected with traditional electronic devices through interfaces, and the visualization of sensor devices can be realized by transmitting signals through Bluetooth technology.

At present, capacitive pressure sensors based on CHs still face many technical problems, such as slow response speeds, low sensitivity, and limited response under high pressure (> 100 kPa). To address these technical issues, Bai et al. [145] developed a capacitive pressure sensor with an ultra-wide pressure sensing range (0.08 Pa–360 kPa), high sensitivity (S_{min}>220 kPa^{-1}), and fast response characteristics (< 20 ms at 1 kHz for the loading of 5 kPa). They formed an efficient dynamic sensing device between the hydrogel and the metal by designing ion–gradient–chargeable microstructures

on I-CHs. Based on this, Xue et al. [120] developed a single-layer composite hydrogel with bulk capacitive junctions by dispersing and adding graphene sheets covered with polypeptides in the gel matrix. They called the hydrogel "SHARK" (single-layer hydrogel artificial skin), which can be used to construct artificial skin with multiple sensing modes. "SHARK" is composed of numerous micro-nanocapacitors dispersed in a gel matrix. It has excellent tensile properties, self-healing abilities, and printable properties. Therefore, this material can be used in finger sensing, acoustic wave sensing, underwater sensing, etc., and has reliable sensing and anti-fatigue properties in different sensing modes and scenarios.

Motion sensors are also a very practical application in daily life. Based on the phenomenon that the deformation of ionic CH only marginally affects electrical conductivity, Cheng et al. [146] pasted the PAM-LiCl CHs onto an elastomer soft robot to achieve the basic function of motion sensing. They measured speed, force, and other information about the robot in the state of fitting and deformation. Inspired by the mechanism of skin coloration by squids, Lin et al. [147] developed a sensing laminate that can be used in visually soft electronics. This sensing laminate is composed of red fluorescent CHs, carbon nanotube film, and polydimethylsiloxane. The microscopic carbon nanotube film combined with the hydrogel laminate can be used as a two-channel soft sensor for monitoring human motion. Ren et al. [141] designed a CH with high toughness (518 kJ/m^3), high ionic conductivity (4.58 S/m), and anti-swelling properties (equilibrium swelling ratio of 9% for 30 days in water). They developed an underwater strain sensor based on its anti-swelling properties and investigated its potential application in underwater motion monitoring. Their research opens new possibilities for developing CH sensors for underwater applications.

Many other potential applications are possible for CHs in the field of instrument science and technology. Li et al. [143] optimized the range of particle transmittance modulation for a temperature-sensitive CH based on PNIPAM-AEMAA (aminoethyl methacrylate). Based on the optimization results, they designed a smart window (as shown in Fig. 10d), which can control the solar energy transmitted through a window to reduce the energy consumption of buildings, contributing to smart-life technology. Similarly, Choe et al. [144] decorated PNIPAM with gold nanoparticles to make raspberry-shaped plasmonic microgels, and they embedded them into PAM hydrogels to construct a smart colorimetric thermometer patch (as shown in Fig. 10e). This new temperature-responsive film enabled fast (1 s) and efficient thermally responsive color changes with a response range of 29–40 °C. It also operated on its own without external power, enabling high sensitivity (0.2 °C) and repeatable temperature monitoring. After PDMS encapsulation, it can be stretched by 90% without showing a color change. This robust, temperature-sensitive, but stretch-insensitive colorimetric temperature-sensing patch can be applied to smart furniture, wearable devices, etc. Generally, the measurement range of CH-based temperature sensors is limited to room temperature to 50 °C; moreover, the sensors are volatile at high temperatures and freeze at sub-zero temperatures. To address this limitation, Li et al. [148] added several additives (glycerol, ethylene glycol, $CaCl_2$, and others) during the preparation of hydrogels, and Liu et al. [149] used a non-volatile column strategy. They all succeeded in extending the temperature sensing range under extreme temperature conditions.

Field of electronic science and technology

The electrical conductivity of CHs makes them useful in the field of electronic science and technology. With their flexibility, high ductility, and transparency, it is possible to make more effective and distinctive electronic circuits and communication devices.

Communication technology is the foundation of research and development in electronic science and technology. In 2013, Keplinger et al. [16] published a study on transparent I-CHs that introduced a large-strain (167% areal strain) actuator with transparent features and a loudspeaker that could generate sound over the entire audible range (as shown in Fig. 11a). Both were fabricated using highly malleable I-CHs developed by their team that are completely transparent to all colors. Yang et al. [150] designed a new axon-like transparent ionic wire to achieve the high-speed transmission of electrical signals (as shown in Fig. 11b). This ionic wire mimics the function of human axons, delivering ionic signals to perception and decision-making systems. It is worth noting that this ion wire can transmit signals with frequencies up to 100 MHz over a range of 10 cm. Communication shielding technology is also a part of communication technology. Liu et al. [151] developed a functionalized ink based on PEDOT:PSS. Through 3D-printing and freeze–thaw strategies, they prepared CHs with high conductivity, a porous structure, and high shape fidelity. This hydrogel exhibited excellent electromagnetic–interference–shielding performance in combination with the internal aqueous environment. They applied it in customized electromagnetic–interference shielding for communication equipment and customized and printed matching shielding equipment according to the geometric shape of the electronic equipment. Their work represents a breakthrough for CHs in the field of electromagnetic–interference–shielding technology for communication devices.

CHs also have applications in brain–machine interfaces (BMIs)—a frontier of scientific research. Due to their biocompatibility and flexibility, CHs can address host immune responses between rigid electronic devices and soft brain tissue. They can also avoid compromising the collection of

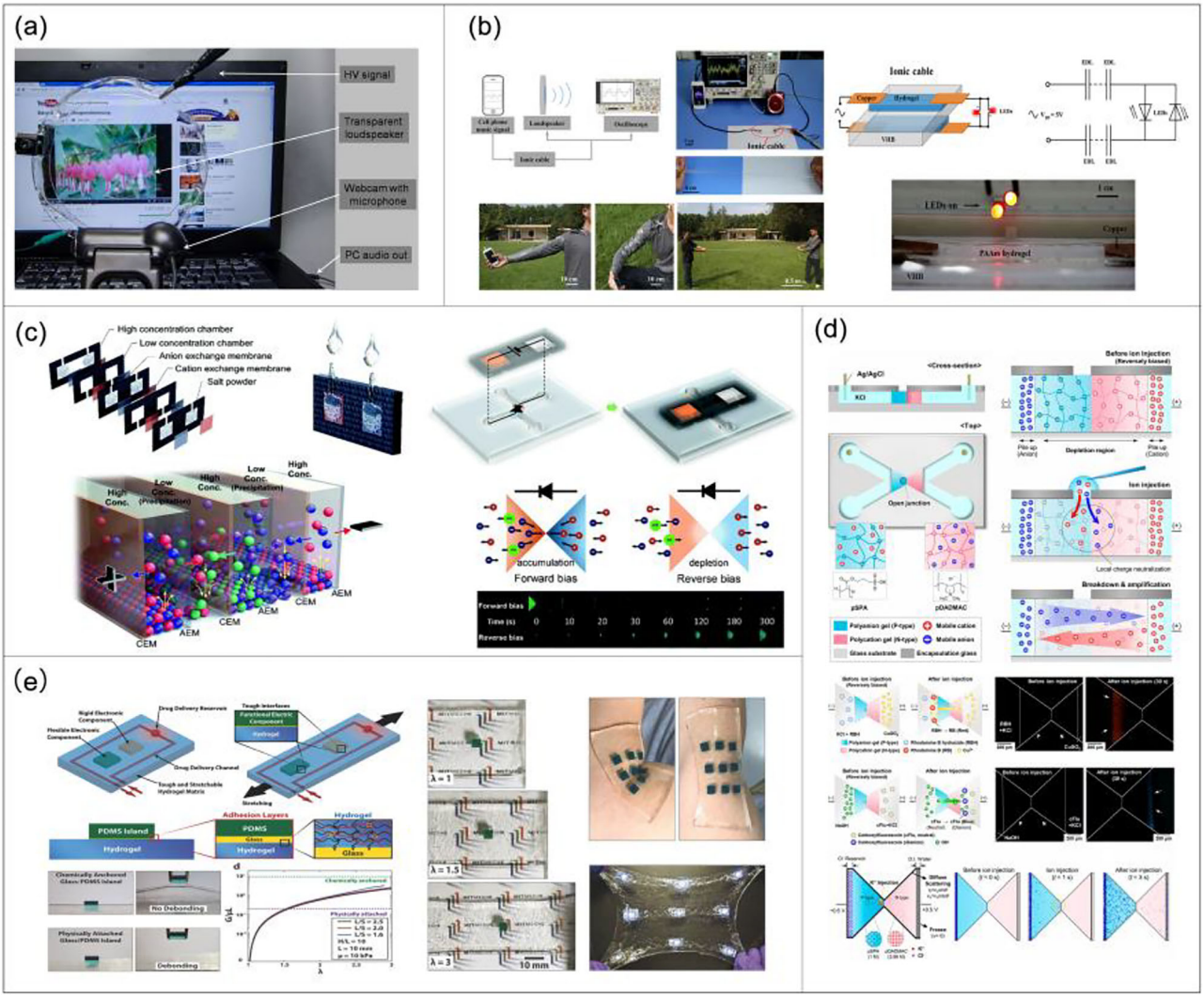

Fig. 11 Applications of CHs in the field of electronic science and technology: **a** the experimental setup for the transparent loudspeaker and the loudspeaker is placed in front of a laptop playing a music video (reproduced from [16], Copyright 2013, with permission from American Association for the Advancement of Science); **b** stretchable, transparent, ionic cable transmits music signal and ionic cable transmits power to turn on light-emitting diodes (reproduced from [150], Copyright 2015, with permission from Elsevier); **c** equivalent circuit and schematic diagram of a polyelectrolyte ionic diode powered by precipitation-assisted solid salt reverse electrodialysis (reproduced from [152], Copyright 2018, with permission from the authors); **d** basic design of open-junction ionic diodes and principle of ion-to-ion amplification and breakdown of the ionic diode by ion injection (reproduced from [153], Copyright 2019, with permission from PNAS); **e** schematic illustration of the design of stretchable hydrogel electronics and devices and integration of rigid chips on the surface of (or inside) a tough hydrogel matrix (reproduced from [154], Copyright 2015, with permission from WILEY–VCH Verlag GmbH & Co. KgaA, Weinheim)

research information and shortening the lifespan of clinical trials in BMI. In 2021, Wang et al. [63] designed a highly conductive hydrogel based on bioelectronics combined with dopamine methacrylate hybrid PEDOT nanoparticles. This hydrogel is extremely adhesive and is able to tightly integrate with metal microcircuits and adhere seamlessly to brain tissue, enabling the fabrication of bioadhesive ultrasoft BMI. More importantly, the material exhibits brain-level modulus and immune evasion, preventing biocompatibility problems with brain tissue and neuroinflammation after implantation. Therefore, hydrogels allow long-term and accurate electroencephalogram signal acquisition and communication with minimal foreign body reaction, something which is very helpful for the development of BMI research.

The application of CHs in electronic circuits is also novel and is rapidly progressing. In essence, CHs can be regarded as a medium for transmitting information, similar to the roles of wires and optical fibers. Their inherent high stretchability enables them to satisfy the needs of stretchable electronic devices—needs that cannot be met by general transmission

media. For these reasons, CHs have been used in electronic-circuit technologies such as semiconductors, circuit boards, and biohybrid computing circuits. Currently, CH-based semiconductors can be divided into two types. CH diodes can be used for signal rectification, and transistors can be used for signal conditioning and amplification. Polyelectrolyte-based CH junctions only allow ionic current to flow in one direction, exhibiting the same effect as diodes [152, 155] (as shown in Fig. 11c), and therefore, can be further applied to wearable ionic circuits. In contrast, CH transistors with open junctions can directly amplify ionic signals [153] (as shown in Fig. 11d). When the P-type and the N-type CHs are arranged face-to-face on the wall of the ion channel, they function as a field-effect transistor that modulates the ion signal. Additionally, Lin et al. [154] found that CHs can maintain the stability of various electronic-circuit elements even under large deformation (as shown in Fig. 11e). This provides a technical reference for the development of stretchable and deformable circuit boards.

Field of biomedical technology

CHs have excellent electrical conductivity and biocompatibility and can be used as cell culture substrates to help complete physiological processes, such as growth and differentiation through electrical signal stimulation. These properties show the effective application of CHs in biomedical fields including tissue engineering, wound dressings, drug release, biosensors, and implantable devices [156–159].

Muscle and neuronal cells in living organisms are sensitive to electrical signals. Therefore, conducting electrical signals with the help of CHs can transmit electrical stimulation or bioelectrical signals generated by cells to other cells and can promote information exchange and material transfer between cells, thereby promoting cell growth, differentiation, and tissue development. These properties have been applied in tissue engineering and wound dressings. For example, a joint team recently developed a PDA-PAM/Mg^{2+} composite antibacterial hydrogel (as shown in Fig. 12a). Under near-infrared radiation, the PDA (polydopamine) component in this composite antibacterial hydrogel has good photothermal efficiency and antibacterial activity. The introduction of Mg^{2+} improves the photostability and recyclability of the photothermal effect, which in turn gives it excellent self-healing and tissue adhesion properties. Therefore, this hydrogel can provide stable and close contact at the wound, which can effectively ensure wound closure to avoid infection, and it has photothermal antibacterial functions that promote wound healing [38]. Tumors are a common and difficult medical problem. Thakor et al. [160] summarized and discussed the application of CH-like materials in brain–tumor–treatment research. CH-based bioengineering approaches can help study the pathophysiology of tumors in vitro and provide new ideas for developing anti-tumor therapeutics. They also highlighted the important application value of hydrogels in bioscaffolds.

CHs have also been used in smart drug sustained release systems. The basic mechanism is to use the response behavior of CHs to electrical signals to control the timing and precise delivery of drugs. In 2018, Qu et al. [161] developed an injectable CH with polyaniline-grafted chitosan and oxidized dextran as the backbone (as shown in Fig. 12b). Experiments showed that this smart drug-loaded CH increased drug release from 34% to 82% from no external field voltage to 3 V external field voltage and has a good smart electrical response control performance. Therefore, injectable and pH-sensitive CHs can be used for controlled drug release in precise doses. Similarly, di Luca et al. [162] prepared a composite CH film with good biocompatibility and electrical responsiveness using gelatin and graphene oxide as the materials. Its hydrophilicity and drug release behavior can be effectively controlled with the stimulation of an applied electric field in the range of 0–48 V. At the same time, it has been found that proteases or cells encapsulated by this membrane retained 80% of their enzymatic activity and more than 94% of their cell viability after delivery and controlled release, which shows great potential for biomedical applications [163]. In addition, Zhao et al. [164] developed an iontophoresis device based on a CH ionic circuit. This device can be used for the efficient intraocular delivery of macromolecules and nanoparticles, enabling non-invasive drug delivery therapy for ocular diseases.

Based on the properties of CHs that allow the hydrogels to respond to multiple external stimuli and convert them into electrical signals, researchers use CHs as the core functional components of biosensors. By combining the two major advantages of controlled drug release and biosensing and supplementing them by advanced manufacturing and packaging processes, soft CH biomedical devices can be implanted into the human body for the real-time monitoring and internal treatment of the affected areas. These implantable devices can monitor fluctuations of various biological signals in real time, such as body temperature, electrocardiograms, blood sugar, and blood pressure, which are key indicators for monitoring human health. The basic mechanism of many existing biosensors is to reflect the health status of the body by detecting analytes (glucose, uric acid, lactic acid, ion level, pH value, and others) in various biological fluids (sweat, tears, saliva, blood, interstitial fluid, etc.). Bariya et al. [165], Heikenfeld et al. [166], Kim et al. [167], Zhao et al. [168], Banerjee et al. [169], and Liu et al. [170] summarized the research and development of wearable biofluid sensors based on CHs, fully verifying the potential application value of wearable biofluid sensors in the biomedical field. They also discussed the challenges and

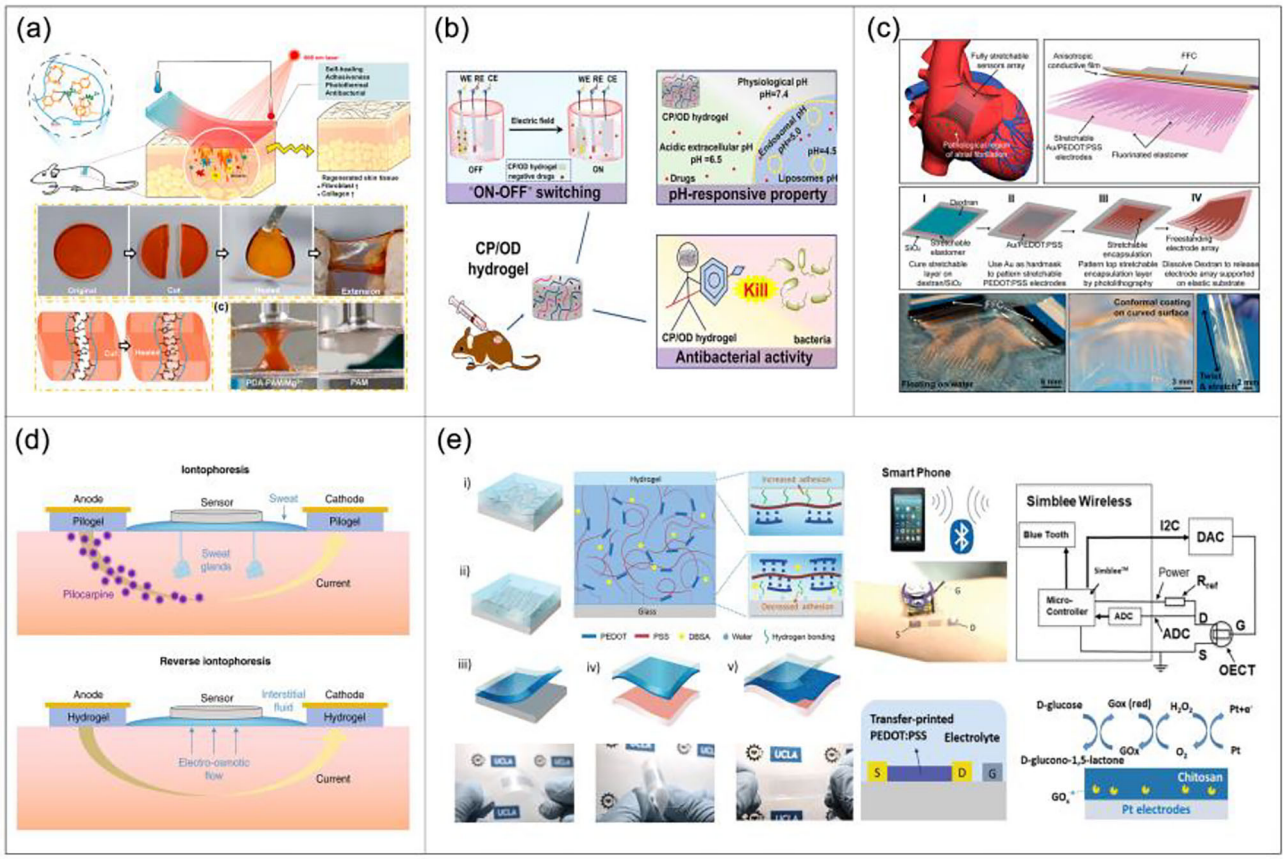

Fig. 12 Applications of CHs in the field of biomedical technology: **a** schematic illustration for the mechanism and application of PDA-PAM/Mg^{2+} hydrogel in wound healing in a full-thickness defect model (reproduced from [38], Copyright 2021, with permission from the authors); **b** schematic illustration for a model of the pulse release of a drug from conductive hydrogel (reproduced from [161], Copyright 2018, with permission from Acta Materialia Inc.); **c** fabrication and assembly of the elastrode array for atrial fibrillation mapping (reproduced from [171], Copyright 2020, with permission from PNAS); **d** schematic of a sweat sensor based on conductive hydrogels (reproduced from [165], Copyright 2018, with permission from the authors); **e** the procedure of our transfer-printing method for PEDOT:PSS films is illustrated in the figure and application diagram of a glucose intelligent monitoring device based on PEDOT:PSS (reproduced from [172], Copyright 2019, with permission from WILEY–VCH Verlag GmbH & Co. KgaA, Weinheim)

opportunities of wearable biofluid sensors in the development of personalized medicine.

As is universally known, the heart is a core organ that ensures the health of the body. Liu et al. [171] developed an organized, high-density, fully elastic microelectrode array based on I-CHs (as shown in Fig. 12c). This microelectrode array can record complex electrophysiological signals and assist electrophysiological mappings in real time and with stability, all with cellular-level resolution in the body. This contributes to uncovering the mechanisms of atrial fibrillation at the cellular level and developing targeted atrial fibrillation therapies. Breathing is also a common, biological monitored target. Wu et al. [173] developed a chemically hygroscopic I-CH with high humidity sensitivity (in the range of 1%–90%) by adding ethylene glycol or glycerol to the PAM hydrogel matrix. This material responds quickly to breathing (0.27 s) and can be used to monitor breathing. Inspired by contact lenses, Elsherif et al. [174] developed a wearable contact lens biosensor based on CH films. This sensor can continuously monitor and quantify blood-glucose indicators under physiological conditions, with a sensitivity of up to 12 nm/mM and a saturation response time of less than 30 min. When the continuous monitoring mode is set, its performance is further improved where the response time is only 3 s and the saturated response time is shortened to 4 min. The device can perform real-time continuous monitoring and diagnosis by being combined with intelligent equipment. Further, the human skin is the easiest part of the body to monitor directly. Ying et al. [175] developed an I-CH with a humidity-sensing capability. It can feed back body information by monitoring changes in the humidity of human skin through four electrical signals (resistance, capacitance,

short-circuit current, and open-circuit voltage). Zhang et al. [172] developed a glucose-monitoring device based on the PEDOT:PSS CHs (as shown in Fig. 12e). They transferred CH films from glass substrates to various flexible substrates using a layering technique, allowing the monitoring device to be directly attached to human skin. This technology has been improved for glucose-responsive wearable insulin patches for blood-glucose monitoring and regulation [176].

Summary and discussion

CHs are exciting, new smart materials. They have the advantages of good conductivity, flexibility, transparency, and biocompatibility, which render them beneficial in the fields of energy and power, instrument science, electronic science, and biomedical technology. To provide a reference for further researchers concerning CHs, this paper reviews the performance characteristics, crosslinking mechanisms, and 3D structure-forming methods of CHs. We discuss the applications of CHs in numerous fields. In the past several years, the study and application of CHs have been gaining in momentum. Through the efforts of many researchers, some excellent results have been achieved, but CHs continue to have strong development prospects. In this section, several issues in the current development of CHs and in possible future development are discussed.

1. Working mechanisms of CHs

The most distinctive features of CHs are their electrical conductivity and accompanying electrical response properties. Current applications of CHs are based on their electrical response properties. Multi-stimulus response properties and multiple working modalities would be an attractive feature if the applications were not limited by their electrical response properties. This enables more innovative research and applications in the fields of multi-response actuating and multi-modal sensing. However, new technical issues will appear. Stimulus introduction with accurate selectivity and the identification of sensing modalities are keys to ensuring the stability and reliability of this innovative work.

2. 3D structure-forming methods of CHs

Currently, the 3D structure-forming methods of CHs are mainly carried out by the in situ curing method and the 3D-printing method. However, these methods have a common technical problem, i.e., the difficult preparation of microstructures. With the development of CHs, there has been a certain demand for microstructure devices. However, the difficulty of their manufacture remains a complex problem. Researchers can learn from microfabrication technology and soft lithography to develop new CH-based 3D structure-forming strategies to build micron-scale CH structures to meet the needs of CH development.

3. Applications of CHs in frontier research fields

Currently, micro-nanorobots are a frontier research field and have broad prospects in both civilian and military applications. The many advantages of CHs make them very suitable for various functional parts and body structures of micro-nanorobots, parts such as intelligent actuators, flexible sensors, and others. In general, there are infinite possibilities for the research and application of micro-nanorobots based on CHs.

Many achievements have been made in the research of CHs in the field of biomedicine, but the scope of application has not reached its potential. At present, there are still some key theoretical and technical problems that need to be solved. For example, the improvement of biocompatibility, biodegradability, stability, and compatibility with the electronic components of CHs are all focuses of biomedical applications.

Supercomputing, big data, artificial intelligence, and other areas represent the current frontiers of technological developments. Computer technology, big data, and artificial intelligence technology based on CHs will be scientific and technological topics of interest. In addition, realizing the integration of CHs with sensing–storage–computing technology is an excellent integration solution. An example would be the case of an intelligent system based on CH semiconductor devices used as the execution device. Then, taking the large amounts of data collected by the CH-based sensing device as the research object, results can be obtained through artificial intelligence technology—enhancing data processing and analysis technology. This combined application can be used in practical scenarios such as in personalized health monitoring, disease prediction, and process deduction.

4. Performance issues that need to be addressed in practical applications of CHs

At present, there are still many problems affecting the practical application of CHs. First, the environmental stability of CHs needs to be improved. We need to find effective methods to control the water loss and structural decay of CHs during long-term storage and usage. Second, we need to improve the stability and reversibility of structure and properties during repeated mechanical deformation. If the above problems can be effectively solved, the application of CHs will be greatly improved.

5. Progress of the practical application of CHs

Although many strong results have been achieved in the research of CHs, there is still a gap between their systematic and popularized applications. The properties of CHs

make them effective for applications in components such as actuators, sensors, communicators, and electronic circuits. However, these applications are only for a single component and research on overall systems is still in its infancy. The systematization of every single component with mature technology will create a qualitative leap in its application potential and value. However, it should be noted that this systematization is not a simple physical combination of stacking CHs, but it is a functional combination sublimation. Moreover, in the process of systematization, the original beneficial characteristics should not be subsumed.

The research and applications of CHs involve many research fields such as materials, biology, mechanics, control, and others. Progress in each field may prompt it achieve a qualitative leap in its research process. Our prediction for the future is that CHs will not only be used in fields such as energy and power technology, but also in space exploration, military reconnaissance, and others.

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Author contributions YH investigated and summarized the literature and wrote the original draft. ZNL completed the analysis of statistical data and the production of the main pictures, and helped revise the paper. ZRL, TJ, and JZS helped revise the paper and gave some advice. YY gave some advice. ZRL, TJ, and JZS supervised the work and applied for funds. All authors have read and approved this manuscript for publication.

Declarations

Conflict of interest The authors declare that there is no conflict of interest.

Ethical approval This study does not contain any studies with human or animal subjects performed by any of the authors.

References

1. Peng Q, Chen J, Wang T et al (2020) Recent advances in designing conductive hydrogels for flexible electronics. InfoMat 2(5):843–865. https://doi.org/10.1002/inf2.12113
2. El-Husseiny HM, Mady EA, Hamabe L et al (2022) Smart/stimuli-responsive hydrogels: cutting-edge platforms for tissue engineering and other biomedical applications. Mater Today Bio 13:100186. https://doi.org/10.1016/j.mtbio.2021.100186
3. Ying B, Liu X (2021) Skin-like hydrogel devices for wearable sensing, soft robotics and beyond. iScience 24(11):103174. https://doi.org/10.1016/j.isci.2021.103174
4. Chun KY, Seo S, Han CS (2022) Wearable all-gel multimodal cutaneous sensor enabling simultaneous single-site monitoring of cardiac-related biophysical signals. Adv Mater 34(16):2110082. https://doi.org/10.1002/adma.202110082
5. Su G, Zhang Y, Zhang X et al (2022) Soft yet tough: a mechanically and functionally tissue-like organohydrogel for sensitive soft electronics. Chem Mater 34(3):1392–1402. https://doi.org/10.1021/acs.chemmater.1c04211
6. Zhang J, Xin W, Qin Y et al (2022) "All-in-one" zwitterionic granular hydrogel bioink for stem cell spheroids production and 3D bioprinting. Chem Eng J 430:132713. https://doi.org/10.1016/j.cej.2021.132713
7. Huang Z, Chen X, O'Neill SJK et al (2022) Highly compressible glass-like supramolecular polymer networks. Nat Mater 21(1):103–109. https://doi.org/10.1038/s41563-021-01124-x
8. Xing ZG, Lin J, Zhao JW (2021) Overview of the artificial muscle actuators. J Mech Eng 57(9):1–11 (in Chinese). https://doi.org/10.3901/JME.2021.09.001
9. Lin Z, Jiang T, Shang J (2021) The emerging technology of biohybrid micro-robots: a review. Bio-Des Manuf 5(1):107–132. https://doi.org/10.1007/s42242-021-00135-6
10. Cheng T, Zhang YZ, Wang S et al (2021) Conductive hydrogel-based electrodes and electrolytes for stretchable and self-healable supercapacitors. Adv Funct Mater 31(24):2101303. https://doi.org/10.1002/adfm.202101303
11. Lu H, Zhang N, Ma M (2019) Electroconductive hydrogels for biomedical applications. WIREs Nanomed Nanobiotechnol 11(6):e1568. https://doi.org/10.1002/wnan.1568
12. Akter M, Bhattacharjee M, Dhar AK et al (2021) Cellulose-based hydrogels for wastewater treatment: a concise review. Gels 7(1):30. https://doi.org/10.3390/gels7010030
13. Alam A, Zhang Y, Kuan HC et al (2018) Polymer composite hydrogels containing carbon nanomaterials—morphology and mechanical and functional performance. Progr Polym Sci 77:1–18. https://doi.org/10.1016/j.progpolymsci.2017.09.001
14. Rong Q, Lei W, Liu M (2018) Conductive hydrogels as smart materials for flexible electronic devices. Chemistry 24(64):16930–16943. https://doi.org/10.1002/chem.201801302
15. English MA, Soenksen LR, Gayet RV et al (2019) Programmable CRISPR-responsive smart materials. Science 365(6455):780–785. https://doi.org/10.1126/science.aaw5122
16. Keplinger C, Sun JY, Foo CC et al (2013) Stretchable, transparent, ionic conductors. Science 341(6149):984–987. https://doi.org/10.1126/science.1240228
17. Deng Y, Huang M, Sun D et al (2018) Dual physically cross-linked κ-carrageenan-based double network hydrogels with superior self-healing performance for biomedical application. ACS Appl Mater Interf 10(43):37544–37554. https://doi.org/10.1021/acsami.8b15385
18. Stojkov G, Niyazov Z, Picchioni F et al (2021) Relationship between structure and rheology of hydrogels for various applications. Gels 7(4):255. https://doi.org/10.3390/gels7040255
19. Wang YJ, Zhang XN, Song Y et al (2019) Ultrastiff and tough supramolecular hydrogels with a dense and robust hydrogen bond network. Chem Mater 31(4):1430–1440. https://doi.org/10.1021/acs.chemmater.8b05262
20. Zhao D, Feng M, Zhang L et al (2021) Facile synthesis of self-healing and layered sodium alginate/polyacrylamide hydrogel promoted by dynamic hydrogen bond. Carbohydr Polym 256:117580. https://doi.org/10.1016/j.carbpol.2020.117580
21. Palmese LL, Thapa RK, Sullivan MO et al (2019) Hybrid hydrogels for biomedical applications. Curr Opin Chem Eng 24:143–157. https://doi.org/10.1016/j.coche.2019.02.010
22. Chang B, Ahuja N, Ma C et al (2017) Injectable scaffolds: preparation and application in dental and craniofacial regeneration. Mater Sci Eng R Rep 111:1–26. https://doi.org/10.1016/j.mser.2016.11.001

23. Liu Q, Nian G, Yang C et al (2018) Bonding dissimilar polymer networks in various manufacturing processes. Nat Commun 9(1):846. https://doi.org/10.1038/s41467-018-03269-x
24. Li S, Wang L, Yu X et al (2018) Synthesis and characterization of a novel double cross-linked hydrogel based on Diels–Alder click reaction and coordination bonding. Mater Sci Eng C Mater Biol Appl 82:299–309. https://doi.org/10.1016/j.msec.2017.08.031
25. Arnfast L, Madsen CG, Jorgensen L et al (2014) Design and processing of nanogels as delivery systems for peptides and proteins. Ther Deliv 5(6):691–708. https://doi.org/10.4155/tde.14.38
26. Wei HL, Yao K, Yang Z et al (2011) Preparation of thermosensitive hydrogels by means of tandem physical and chemical crosslinking. Macromol Res 19(3):294–299. https://doi.org/10.1007/s13233-011-0308-z
27. Shao C, Chang H, Wang M et al (2017) High-strength, tough, and self-healing nanocomposite physical hydrogels based on the synergistic effects of dynamic hydrogen bond and dual coordination bonds. ACS Appl Mater Interf 9(34):28305–28318. https://doi.org/10.1021/acsami.7b09614
28. Mredha MTI, Pathak SK, Tran VT et al (2019) Hydrogels with superior mechanical properties from the synergistic effect in hydrophobic–hydrophilic copolymers. Chem Eng J 362:325–338. https://doi.org/10.1016/j.cej.2018.12.023
29. Oveissi F, Naficy S, Le TYL et al (2018) Tough and processable hydrogels based on lignin and hydrophilic polyurethane. ACS Appl Bio Mater 1(6):2073–2081. https://doi.org/10.1021/acsabm.8b00546
30. Deng Y, Hussain I, Kang M et al (2018) Self-recoverable and mechanical-reinforced hydrogel based on hydrophobic interaction with self-healable and conductive properties. Chem Eng J 353:900–910. https://doi.org/10.1016/j.cej.2018.07.187
31. Zhang XN, Wang YJ, Sun S et al (2018) A tough and stiff hydrogel with tunable water content and mechanical properties based on the synergistic effect of hydrogen bonding and hydrophobic interaction. Macromolecules 51(20):8136–8146. https://doi.org/10.1021/acs.macromol.8b01496
32. Chang X, Geng Y, Cao H et al (2018) Dual-crosslink physical hydrogels with high toughness based on synergistic hydrogen bonding and hydrophobic interactions. Macromol Rapid Commun 39(14):e1700806. https://doi.org/10.1002/marc.201700806
33. Liang Y, Xue J, Du B et al (2019) Ultrastiff, tough, and healable ionic-hydrogen bond cross-linked hydrogels and their uses as building blocks to construct complex hydrogel structures. ACS Appl Mater Interf 11(5):5441–5454. https://doi.org/10.1021/acsami.8b20520
34. Lin Y, Zhang H, Liao H et al (2019) A physically crosslinked, self-healing hydrogel electrolyte for nano-wire PANI flexible supercapacitors. Chem Eng J 367:139–148. https://doi.org/10.1016/j.cej.2019.02.064
35. Liu S, Oderinde O, Hussain I (2018) Dual ionic cross-linked double network hydrogel with self-healing, conductive, and force sensitive properties. Polymer 144:111–120. https://doi.org/10.1016/j.polymer.2018.01.046
36. Mondal S, Das S, Nandi AK (2020) A review on recent advances in polymer and peptide hydrogels. Soft Matter 16(6):1404–1454. https://doi.org/10.1039/c9sm02127b
37. Dai X, Zhang Y, Gao L et al (2015) A mechanically strong, highly stable, thermoplastic, and self-healable supramolecular polymer hydrogel. Adv Mater 27(23):3566–3571. https://doi.org/10.1002/adma.201500534
38. Guo Z, Zhang Z, Zhang N et al (2021) A Mg^{2+}/polydopamine composite hydrogel for the acceleration of infected wound healing. Bioact Mater 15:203–213. https://doi.org/10.1016/j.bioactmat.2021.11.036
39. Zhang M, Yin Q, Ji X et al (2020) High and fast adsorption of Cd(II) and Pb(II) ions from aqueous solutions by a waste biomass based hydrogel. Sci Rep 10(1):3285. https://doi.org/10.1038/s41598-020-60160-w
40. Zhu H, Hu X, Liu B et al (2021) 3D printing of conductive hydrogel-elastomer hybrids for stretchable electronics. ACS Appl Mater Interf 13(49):59243–59251. https://doi.org/10.1021/acsami.1c17526
41. Jiang H, Duan L, Ren X et al (2019) Hydrophobic association hydrogels with excellent mechanical and self-healing properties. Eur Polym J 112:660–669. https://doi.org/10.1016/j.eurpolymj.2018.10.031
42. Zhou Y, Zhao S, Zhang C et al (2018) Photopolymerized maleilated chitosan/thiol-terminated poly (vinyl alcohol) hydrogels as potential tissue engineering scaffolds. Carbohydr Polym 184:383–389. https://doi.org/10.1016/j.carbpol.2018.01.009
43. Brown TE, Carberry BJ, Worrell BT et al (2018) Photopolymerized dynamic hydrogels with tunable viscoelastic properties through thioester exchange. Biomaterials 178:496–503. https://doi.org/10.1016/j.biomaterials.2018.03.060
44. Zhou Y, Liang K, Zhao S et al (2018) Photopolymerized maleilated chitosan/methacrylated silk fibroin micro/nanocomposite hydrogels as potential scaffolds for cartilage tissue engineering. Int J Biol Macromol 108:383–390. https://doi.org/10.1016/j.ijbiomac.2017.12.032
45. Zhong Y, Wang J, Yuan Z et al (2019) A mussel-inspired carboxymethyl cellulose hydrogel with enhanced adhesiveness through enzymatic crosslinking. Colloids Surf B Biointerf 179:462–469. https://doi.org/10.1016/j.colsurfb.2019.03.044
46. Kim SH, Kim K, Kim BS et al (2020) Fabrication of polyphenol-incorporated anti-inflammatory hydrogel via high-affinity enzymatic crosslinking for wet tissue adhesion. Biomaterials 242:119905. https://doi.org/10.1016/j.biomaterials.2020.119905
47. Wei Q, Duan J, Ma G et al (2019) Enzymatic crosslinking to fabricate antioxidant peptide-based supramolecular hydrogel for improving cutaneous wound healing. J Mater Chem B 7(13):2220–2225. https://doi.org/10.1039/c8tb03147a
48. Wang H, Zhu D, Paul A et al (2017) Covalently adaptable elastin-like protein−hyaluronic acid (ELP−HA) hybrid hydrogels with secondary thermoresponsive crosslinking for injectable stem cell delivery. Adv Funct Mater 27(28):1605609. https://doi.org/10.1002/adfm.201605609
49. Shin JY, Yeo YH, Jeong JE et al (2020) Dual-crosslinked methylcellulose hydrogels for 3D bioprinting applications. Carbohydr Polym 238:116192. https://doi.org/10.1016/j.carbpol.2020.116192
50. Wang Y, Ma M, Wang J et al (2018) Development of a photocrosslinking, biodegradable GelMA/PEGDA hydrogel for guided bone regeneration materials. Materials 11(8):1345. https://doi.org/10.3390/ma11081345
51. Kim HH, Kim JW, Choi J et al (2018) Characterization of silk hydrogel formed with hydrolyzed silk fibroin-methacrylate via photopolymerization. Polymer 153:232–240. https://doi.org/10.1016/j.polymer.2018.08.019
52. Spearman BS, Agrawal NK, Rubiano A et al (2020) Tunable methacrylated hyaluronic acid-based hydrogels as scaffolds for soft tissue engineering applications. J Biomed Mater Res A 108(2):279–291. https://doi.org/10.1002/jbm.a.36814
53. Xiao W, Qu X, Li J et al (2019) Synthesis and characterization of cell-laden double-network hydrogels based on silk fibroin and methacrylated hyaluronic acid. Eur Polym J 118:382–392. https://doi.org/10.1016/j.eurpolymj.2019.05.040
54. Teixeira LS, Feijen J, van Blitterswijk CA et al (2012) Enzyme-catalyzed crosslinkable hydrogels: emerging strategies for tissue engineering. Biomaterials 33(5):1281–1290. https://doi.org/10.1016/j.biomaterials.2011.10.067

55. Ranga A, Lutolf MP, Hilborn J et al (2016) Hyaluronic acid hydrogels formed in situ by transglutaminase-catalyzed reaction. Biomacromolecules 17(5):1553–1560. https://doi.org/10.1021/acs.biomac.5b01587
56. Parada GA, Yuk H, Liu X et al (2017) Impermeable robust hydrogels via hybrid lamination. Adv Healthc Mater 6(19):1700520. https://doi.org/10.1002/adhm.201700520
57. Hennink WE, van Nostrum CF (2012) Novel crosslinking methods to design hydrogels. Adv Drug Deliv Rev 64:223–236. https://doi.org/10.1016/j.addr.2012.09.009
58. Deng Z, Wang H, Ma PX et al (2020) Self-healing conductive hydrogels: preparation, properties and applications. Nanoscale 12(3):1224–1246. https://doi.org/10.1039/c9nr09283h
59. Mauri E, Negri A, Rebellato E et al (2018) Hydrogel-nanoparticles composite system for controlled drug delivery. Gels 4(3):74. https://doi.org/10.3390/gels4030074
60. Onaciu A, Munteanu RA, Moldovan AI et al (2019) Hydrogels based drug delivery synthesis, characterization and administration. Pharmaceutics 11(9):432. https://doi.org/10.3390/pharmaceutics11090432
61. Wang K, Hao Y, Wang Y et al (2019) Functional hydrogels and their application in drug delivery, biosensors, and tissue engineering. Int J Polym Sci 2019:1–14. https://doi.org/10.1155/2019/3160732
62. Han L, Yan L, Wang M et al (2018) Transparent, adhesive, and conductive hydrogel for soft bioelectronics based on light-transmitting polydopamine-doped polypyrrole nanofibrils. Chem Mater 30(16):5561–5572. https://doi.org/10.1021/acs.chemmater.8b01446
63. Wang X, Sun X, Gan D et al (2022) Bioadhesive and conductive hydrogel-integrated brain-machine interfaces for conformal and immune-evasive contact with brain tissue. Matter 5(4):1204–1223. https://doi.org/10.1016/j.matt.2022.01.012
64. Rothemund P, Kellaris N, Mitchell SK et al (2021) HASEL artificial muscles for a new generation of lifelike robots-recent progress and future opportunities. Adv Mater 33(19):e2003375. https://doi.org/10.1002/adma.202003375
65. Ha JH, Shin HH, Choi HW et al (2020) Electro-responsive hydrogel-based microfluidic actuator platform for photothermal therapy. Lab Chip 20(18):3354–3364. https://doi.org/10.1039/d0lc00458h
66. Song X, Wang C, Chen J et al (2021) Unraveling the synergistic coupling mechanism of Li^+ transport in an "Ionogel-in-Ceramic" hybrid solid electrolyte for rechargeable lithium metal battery. Adv Funct Mater 32(10):2108706. https://doi.org/10.1002/adfm.202108706
67. Cheng FM, Chen HX, Li HD (2020) Recent advances in tough and self-healing nanocomposite hydrogels for shape morphing and soft actuators. Eur Polym J 124:109448. https://doi.org/10.1016/j.eurpolymj.2019.109448
68. Fantino E, Chiappone A, Roppolo I et al (2016) 3D printing of conductive complex structures with in situ generation of silver nanoparticles. Adv Mater 28(19):3712–3717. https://doi.org/10.1002/adma.201505109
69. Baei P, Jalili-Firoozinezhad S, Rajabi-Zeleti S et al (2016) Electrically conductive gold nanoparticle-chitosan thermosensitive hydrogels for cardiac tissue engineering. Mater Sci Eng C Mater Biol Appl 63:131–141. https://doi.org/10.1016/j.msec.2016.02.056
70. Navaei A, Saini H, Christenson W et al (2016) Gold nanorod-incorporated gelatin-based conductive hydrogels for engineering cardiac tissue constructs. Acta Biomater 41:133–146. https://doi.org/10.1016/j.actbio.2016.05.027
71. Walker BW, Lara RP, Mogadam E et al (2019) Rational design of microfabricated electroconductive hydrogels for biomedical applications. Prog Polym Sci 92:135–157. https://doi.org/10.1016/j.progpolymsci.2019.02.007
72. Liang Y, Zhao X, Hu T et al (2019) Mussel-inspired, antibacterial, conductive, antioxidant, injectable composite hydrogel wound dressing to promote the regeneration of infected skin. J Colloid Interf Sci 556:514–528. https://doi.org/10.1016/j.jcis.2019.08.083
73. Liang Y, Zhao X, Hu T et al (2019) Adhesive hemostatic conducting injectable composite hydrogels with sustained drug release and photothermal antibacterial activity to promote full-thickness skin regeneration during wound healing. Small 15(12):e1900046. https://doi.org/10.1002/smll.201900046
74. Zhou Y, Fei X, Tian J et al (2022) A ionic liquid enhanced conductive hydrogel for strain sensing applications. J Colloid Interf Sci 606(Pt 1):192–203. https://doi.org/10.1016/j.jcis.2021.07.158
75. Dong R, Ma PX, Guo B (2020) Conductive biomaterials for muscle tissue engineering. Biomaterials 229:119584. https://doi.org/10.1016/j.biomaterials.2019.119584
76. Chakraborty P, Guterman T, Adadi N et al (2019) A self-healing, all-organic, conducting, composite peptide hydrogel as pressure sensor and electrogenic cell soft substrate. ACS Nano 13(1):163–175. https://doi.org/10.1021/acsnano.8b05067
77. Wang W, Narain R, Zeng H (2018) Rational design of self-healing tough hydrogels: a mini review. Front Chem 6:497. https://doi.org/10.3389/fchem.2018.00497
78. Guo Q, Chen J, Wang J et al (2020) Recent progress in synthesis and application of mussel-inspired adhesives. Nanoscale 12(3):1307–1324. https://doi.org/10.1039/c9nr09780e
79. Zhang G, Yang Y, Chen Y et al (2018) A quadruple-hydrogen-bonded supramolecular binder for high-performance silicon anodes in lithium-ion batteries. Small 14(29):e1801189. https://doi.org/10.1002/smll.201801189
80. Yi H, Lan T, Yang Y et al (2018) Aqueous-processable polymer binder with strong mechanical and polysulfide-trapping properties for high performance of lithium–sulfur batteries. J Mater Chem A 6(38):18660–18668. https://doi.org/10.1039/c8ta07194b
81. Huang W, Wang Y, Huang Z et al (2018) On-demand dissolvable self-healing hydrogel based on carboxymethyl chitosan and cellulose nanocrystal for deep partial thickness burn wound healing. ACS Appl Mater Interf 10(48):41076–41088. https://doi.org/10.1021/acsami.8b14526
82. Devaki SJ, Narayanan RK, Sarojam S (2014) Electrically conducting silver nanoparticle–polyacrylic acid hydrogel by in situ reduction and polymerization approach. Mater Lett 116:135–138. https://doi.org/10.1016/j.matlet.2013.10.110
83. Hyun DC, Park M, Park C et al (2011) Ordered zigzag stripes of polymer gel/metal nanoparticle composites for highly stretchable conductive electrodes. Adv Mater 23(26):2946–2950. https://doi.org/10.1002/adma.201100639
84. Han L, Liu K, Wang M et al (2018) Mussel-inspired adhesive and conductive hydrogel with long-lasting moisture and extreme temperature tolerance. Adv Funct Mater 28(3):1704195. https://doi.org/10.1002/adfm.201704195
85. Mottet L, Le Cornec D, Noel JM et al (2018) A conductive hydrogel based on alginate and carbon nanotubes for probing microbial electroactivity. Soft Matter 14(8):1434–1441. https://doi.org/10.1039/c7sm01929g
86. Lin X, Li F, Bing Y et al (2021) Biocompatible multifunctional e-skins with excellent self-healing ability enabled by clean and scalable fabrication. Nanomicro Lett 13(1):200. https://doi.org/10.1007/s40820-021-00701-8
87. Ilami M, Bagheri H, Ahmed R et al (2021) Materials, actuators, and sensors for soft bioinspired robots. Adv Mater 33(19):e2003139. https://doi.org/10.1002/adma.202003139

88. Lu B, Yuk H, Lin S et al (2019) Pure PEDOT:PSS hydrogels. Nat Commun 10(1):1043. https://doi.org/10.1038/s41467-019-09003-5
89. Yang C, Suo Z (2018) Hydrogel ionotronics. Nat Rev Mater 3(6):125–142. https://doi.org/10.1038/s41578-018-0018-7
90. Bai Y, Chen B, Xiang F et al (2014) Transparent hydrogel with enhanced water retention capacity by introducing highly hydratable salt. Appl Phys Lett 105:151903. https://doi.org/10.1063/1.4898189
91. Wang H, Zhu B, Jiang W et al (2014) A mechanically and electrically self-healing supercapacitor. Adv Mater 26(22):3638–3643. https://doi.org/10.1002/adma.201305682
92. Huang Y, Zhong M, Shi F et al (2017) An intrinsically stretchable and compressible supercapacitor containing a polyacrylamide hydrogel electrolyte. Angew Chem Int Ed Engl 56(31):9141–9145. https://doi.org/10.1002/anie.201705212
93. Zhao F, Bae J, Zhou X et al (2018) Nanostructured functional hydrogels as an emerging platform for advanced energy technologies. Adv Mater 30(48):e1801796. https://doi.org/10.1002/adma.201801796
94. Chen B, Chen Q, Xiao S et al (2021) Giant negative thermopower of ionic hydrogel by synergistic coordination and hydration interactions. Sci Adv 7(48):eabi7233. https://doi.org/10.1126/sciadv.abi7233
95. Huang Y, Li H, Wang Z et al (2016) Nanostructured polypyrrole as a flexible electrode material of supercapacitor. Nano Energy 22:422–438. https://doi.org/10.1016/j.nanoen.2016.02.047
96. Huo Z, Tao L, Wang S et al (2015) A novel polysulfide hydrogel electrolyte based on low molecular mass organogelator for quasi-solid-state quantum dot-sensitized solar cells. J Power Sources 284:582–587. https://doi.org/10.1016/j.jpowsour.2015.03.049
97. Kellaris N, Gopaluni Venkata V, Smith Garrett M et al (2018) Peano-HASEL actuators: muscle-mimetic, electrohydraulic transducers that linearly contract on activation. Sci Robot 3(14):eaar3276. https://doi.org/10.1126/scirobotics.aar3276
98. Sun JY, Keplinger C, Whitesides GM et al (2014) Ionic skin. Adv Mater 26(45):7608–7614. https://doi.org/10.1002/adma.201403441
99. Li T, Li G, Liang Y et al (2017) Fast-moving soft electronic fish. Sci Adv 3(4):e1602045. https://doi.org/10.1126/sciadv.1602045
100. Yang H, Li C, Yang M et al (2019) Printing hydrogels and elastomers in arbitrary sequence with strong adhesion. Adv Funct Mater 29(27):1901721. https://doi.org/10.1002/adfm.201901721
101. Lei Z, Wang Q, Wu P (2017) A multifunctional skin-like sensor based on a 3D printed thermo-responsive hydrogel. Mater Horiz 4(4):694–700. https://doi.org/10.1039/c7mh00262a
102. Haghiashtiani G, Habtour E, Park SH et al (2018) 3D printed electrically-driven soft actuators. Extreme Mech Lett 21:1–8. https://doi.org/10.1016/j.eml.2018.02.002
103. Cheng FM, Chen HX, Li HD (2021) Recent progress on hydrogel actuators. J Mater Chem B 9(7):1762–1780. https://doi.org/10.1039/d0tb02524k
104. Jiang T, Munguia-Lopez JG, Flores-Torres S et al (2017) Directing the self-assembly of tumour spheroids by bioprinting cellular heterogeneous models within alginate/gelatin hydrogels. Sci Rep 7(1):4575. https://doi.org/10.1038/s41598-017-04691-9
105. Jiang T, Munguia-Lopez J, Flores-Torres S et al (2018) Bioprintable alginate/gelatin hydrogel 3D in vitro model systems induce cell spheroid formation. J Vis Exp 137:e57826. https://doi.org/10.3791/57826
106. Jiang T, Munguia-Lopez JG, Gu K et al (2019) Engineering bioprintable alginate/gelatin composite hydrogels with tunable mechanical and cell adhesive properties to modulate tumor spheroid growth kinetics. Biofabrication 12(1):015024. https://doi.org/10.1088/1758-5090/ab3a5c
107. Lin Z, Jiang T, Kinsella JM et al (2021) Assessing roughness of extrusion printed soft materials using a semi-quantitative method. Mater Lett 303:130480. https://doi.org/10.1016/j.matlet.2021.130480
108. Acome E, Mitchell SK, Morrissey TG et al (2018) Hydraulically amplified self-healing electrostatic actuators with muscle-like performance. Science 359(6371):61–65. https://doi.org/10.1126/science.aao6139
109. Mitchell SK, Wang X, Acome E et al (2019) An easy-to-implement toolkit to create versatile and high-performance HASEL actuators for untethered soft robots. Adv Sci 6(14):1900178. https://doi.org/10.1002/advs.201900178
110. Tian K, Bae J, Bakarich SE et al (2017) 3D printing of transparent and conductive heterogeneous hydrogel-elastomer systems. Adv Mater 29(10):1604827. https://doi.org/10.1002/adma.201604827
111. Yuk H, Lu B, Lin S et al (2020) 3D printing of conducting polymers. Nat Commun 11(1):1604. https://doi.org/10.1038/s41467-020-15316-7
112. Zhou LY, Fu J, He Y (2020) A review of 3D printing technologies for soft polymer materials. Adv Funct Mater 30(28):2000187. https://doi.org/10.1002/adfm.202000187
113. Handral HK, Natu VP, Cao T et al (2022) Emerging trends and prospects of electroconductive bioinks for cell-laden and functional 3D bioprinting. Bio-Des Manuf 5(2):396–411. https://doi.org/10.1007/s42242-021-00169-w
114. Jiang T, Munguia-Lopez JG, Flores-Torres S et al (2019) Extrusion bioprinting of soft materials: an emerging technique for biological model fabrication. Appl Phys Rev 6(1):011310. https://doi.org/10.1063/1.5059393
115. Ying GL, Jiang N, Maharjan S et al (2018) Aqueous two-phase emulsion bioink-enabled 3D bioprinting of porous hydrogels. Adv Mater 30(50):e1805460. https://doi.org/10.1002/adma.201805460
116. Truby RL, Wehner M, Grosskopf AK et al (2018) Soft somatosensitive actuators via embedded 3D printing. Adv Mater 30(15):e1706383. https://doi.org/10.1002/adma.201706383
117. Shao L, Gao Q, Xie C et al (2020) Synchronous 3D bioprinting of large-scale cell-laden constructs with nutrient networks. Adv Healthc Mater 9(15):e1901142. https://doi.org/10.1002/adhm.201901142
118. Shao L, Gao Q, Xie C et al (2020) Sacrificial microgel-laden bioink-enabled 3D bioprinting of mesoscale pore networks. Bio-Des Manuf 3(1):30–39. https://doi.org/10.1007/s42242-020-00062-y
119. Dong Z, Vuckovac M, Cui W et al (2021) 3D printing of superhydrophobic objects with bulk nanostructure. Adv Mater 33(45):e2106068. https://doi.org/10.1002/adma.202106068
120. Xue B, Sheng H, Li Y et al (2021) Stretchable and self-healable hydrogel artificial skin. Nat Sci Rev (Early Access). https://doi.org/10.1093/nsr/nwab147
121. Naficy S, Razal JM, Spinks GM et al (2012) Electrically conductive, tough hydrogels with pH sensitivity. Chem Mater 24(17):3425–3433. https://doi.org/10.1021/cm301666w
122. Liang X, Chen G, Lin S et al (2022) Bioinspired 2D isotropically fatigue-resistant hydrogels. Adv Mater 34(8):e2107106. https://doi.org/10.1002/adma.202107106
123. Guo G, Wu Q, Liu F et al (2021) Solvent-cast-assisted printing of biomimetic morphing hydrogel structures with solvent evaporation-induced swelling mismatch. Adv Funct Mater 32(2):2108548. https://doi.org/10.1002/adfm.202108548
124. Yuk H, Zhang T, Parada GA et al (2016) Skin-inspired hydrogel-elastomer hybrids with robust interfaces and functional microstructures. Nat Commun 7(1):12028. https://doi.org/10.1038/ncomms12028

125. Pissis P, Kyritsis A (1997) Electrical conductivity studies in hydrogels. Solid State Ion 97(1–4):105–113. https://doi.org/10.1016/s0167-2738(97)00074-x
126. Kaklamani G, Kazaryan D, Bowen J et al (2018) On the electrical conductivity of alginate hydrogels. Regen Biomater 5(5):293–301. https://doi.org/10.1093/rb/rby019
127. Chandra H, Allen SW, Oberloier SW et al (2017) Open-source automated mapping four-point probe. Materials 10(2):110. https://doi.org/10.3390/ma10020110
128. Zhao X, Chen F, Li Y et al (2018) Bioinspired ultra-stretchable and anti-freezing conductive hydrogel fibers with ordered and reversible polymer chain alignment. Nat Commun 9(1):3579. https://doi.org/10.1038/s41467-018-05904-z
129. Niiyama R, Rus D, Kim S (2014) Pouch motors: printable/inflatable soft actuators for robotics. In: IEEE international conference on robotics and automation, pp 6332–6337. https://doi.org/10.1109/ICRA.2014.6907793
130. Sanan S, Lynn PS, Griffith ST (2014) Pneumatic torsional actuators for inflatable robots. J Mech Robot 6(3):031003. https://doi.org/10.1115/1.4026629
131. Li W, Gao F, Wang X et al (2016) Strong and robust polyaniline-based supramolecular hydrogels for flexible supercapacitors. Angew Chem Int Ed Engl 55(32):9196–9201. https://doi.org/10.1002/anie.201603417
132. Li W, Lu H, Zhang N et al (2017) Enhancing the properties of conductive polymer hydrogels by freeze-thaw cycles for high-performance flexible supercapacitors. ACS Appl Mater Interf 9(23):20142–20149. https://doi.org/10.1021/acsami.7b05963
133. Chen Q, Lu H, Chen F et al (2018) Supramolecular hydrogels for high-voltage and neutral-ph flexible supercapacitors. ACS Appl Energy Mater 1(8):4261–4268. https://doi.org/10.1021/acsaem.8b00891
134. Lu H, Li Y, Chen Q et al (2019) Semicrystalline conductive hydrogels for high-energy and stable flexible supercapacitors. ACS Appl Energy Mater 2(11):8163–8172. https://doi.org/10.1021/acsaem.9b01629
135. Chen F, Chen Q, Song Q et al (2019) Strong and stretchable polypyrrole hydrogels with biphase microstructure as electrodes for substrate-free stretchable supercapacitors. Appl Mater Interf 6(11):1900133. https://doi.org/10.1002/admi.201900133
136. Pu X, Liu M, Chen X et al (2017) Ultrastretchable, transparent triboelectric nanogenerator as electronic skin for biomechanical energy harvesting and tactile sensing. Sci Adv 3(5):e1700015. https://doi.org/10.1126/sciadv.1700015
137. Zhou Y, Hou Y, Li Q et al (2017) Biocompatible and flexible hydrogel diode-based mechanical energy harvesting. Adv Mater Technol 2(9):1700118. https://doi.org/10.1002/admt.201700118
138. Parida K, Kumar V, Wang JX et al (2017) Highly transparent, stretchable, and self-healing ionic-skin triboelectric nanogenerators for energy harvesting and touch applications. Adv Mater 29(37):1702181. https://doi.org/10.1002/adma.201702181
139. Zhou D, Chen F, Handschuh-Wang S et al (2019) Biomimetic extreme-temperature- and environment-adaptable hydrogels. ChemPhysChem 20(17):2139–2154. https://doi.org/10.1002/cphc.201900545
140. Zhang S, Wang F, Peng H et al (2018) Flexible highly sensitive pressure sensor based on ionic liquid gel film. ACS Omega 3(3):3014–3021. https://doi.org/10.1021/acsomega.7b01575
141. Ren J, Liu Y, Wang Z et al (2021) An anti-swellable hydrogel strain sensor for underwater motion detection. Adv Funct Mater 32(13):2107404. https://doi.org/10.1002/adfm.202107404
142. Sarwar MS, Dobashi Y, Preston C et al (2017) Bend, stretch, and touch: locating a finger on an actively deformed transparent sensor array. Sci Adv 3(3):e1602200. https://doi.org/10.1126/sciadv.1602200
143. Li XH, Liu C, Feng SP et al (2019) Broadband light management with thermochromic hydrogel microparticles for smart windows. Joule 3(1):290–302. https://doi.org/10.1016/j.joule.2018.10.019
144. Choe A, Yeom J, Shanker R et al (2018) Stretchable and wearable colorimetric patches based on thermoresponsive plasmonic microgels embedded in a hydrogel film. NPG Asia Mater 10(9):912–922. https://doi.org/10.1038/s41427-018-0086-6
145. Bai N, Wang L, Wang Q et al (2020) Graded intrafillable architecture-based iontronic pressure sensor with ultra-broad-range high sensitivity. Nat Commun 11(1):209. https://doi.org/10.1038/s41467-019-14054-9
146. Cheng S, Narang YS, Yang C et al (2019) Stick-on large-strain sensors for soft robots. Adv Mater Interf 6(20):1900985. https://doi.org/10.1002/admi.201900985
147. Lin G, Si M, Wang L et al (2022) Dual-channel flexible strain sensors based on mechanofluorescent and conductive hydrogel laminates. Adv Opt Mater 10(5):2102306. https://doi.org/10.1002/adom.202102306
148. Li Y, Hu CX, Lan J et al (2020) Hydrogel-based temperature sensor with water retention, frost resistance and remoldability. Polymer 186:122027. https://doi.org/10.1016/j.polymer.2019.122027
149. Liu Z, Wang Y, Ren Y et al (2020) Poly(ionic liquid) hydrogel-based anti-freezing ionic skin for a soft robotic gripper. Maters Horiz 7(3):919–927. https://doi.org/10.1039/c9mh01688k
150. Yang CH, Chen B, Lu JJ et al (2015) Ionic cable. Extreme Mech Lett 3:59–65. https://doi.org/10.1016/j.eml.2015.03.001
151. Liu J, McKeon L, Garcia J et al (2022) Additive manufacturing of Ti_3C_2-MXene-functionalized conductive polymer hydrogels for electromagnetic-interference shielding. Adv Mater 34(5):e2106253. https://doi.org/10.1002/adma.202106253
152. Yeon SY, Yun J, Yoon SH et al (2018) A miniaturized solid salt reverse electrodialysis battery: a durable and fully ionic power source. Chem Sci 9(42):8071–8076. https://doi.org/10.1039/c8sc02954g
153. Lim SM, Yoo H, Oh MA et al (2019) Ion-to-ion amplification through an open-junction ionic diode. Proc Natl Acad Sci USA 116(28):13807–13815. https://doi.org/10.1073/pnas.1903900116
154. Lin S, Yuk H, Zhang T et al (2016) Stretchable hydrogel electronics and devices. Adv Mater 28(22):4497–4505. https://doi.org/10.1002/adma.201504152
155. Lee HR, Woo J, Han SH et al (2019) A stretchable ionic diode from copolyelectrolyte hydrogels with methacrylated polysaccharides. Adv Funct Mater 29(4):1806909. https://doi.org/10.1002/adfm.201806909
156. Bai R, Yang J, Morelle XP et al (2018) Fatigue fracture of self-recovery hydrogels. ACS Macro Lett 7(3):312–317. https://doi.org/10.1021/acsmacrolett.8b00045
157. Huang S, Liu Y, Zhao Y et al (2018) Flexible electronics: stretchable electrodes and their future. Adv Funct Mater 29(6):1805924. https://doi.org/10.1002/adfm.201805924
158. Vazquez-Gonzalez M, Willner I (2020) Stimuli-responsive biomolecule-based hydrogels and their applications. Angew Chem Int Ed Engl 59(36):15342–15377. https://doi.org/10.1002/anie.201907670
159. Wang J, Wang Z, Yu J et al (2020) Glucose-responsive insulin and delivery systems: innovation and translation. Adv Mater 32(13):e1902004. https://doi.org/10.1002/adma.201902004
160. Thakor J, Ahadian S, Niakan A et al (2020) Engineered hydrogels for brain tumor culture and therapy. Bio-Des Manuf 3(3):203–226. https://doi.org/10.1007/s42242-020-00084-6
161. Qu J, Zhao X, Ma PX et al (2018) Injectable antibacterial conductive hydrogels with dual response to an electric field and pH for localized "smart" drug release. Acta Biomater 72:55–69. https://doi.org/10.1016/j.actbio.2018.03.018

162. di Luca M, Vittorio O, Cirillo G et al (2018) Electro-responsive graphene oxide hydrogels for skin bandages: the outcome of gelatin and trypsin immobilization. Int J Pharm 546(1–2):50–60. https://doi.org/10.1016/j.ijpharm.2018.05.027
163. Fan Z, Cheng P, Zhang D et al (2020) Progress on stimulus responsive smart hydrogels based on natural polymers. Mater Rep 34(21):21012–21025 (in Chinese). https://doi.org/10.11896/cldb.19080216
164. Zhao F, Fan S, Ghate D et al (2022) A hydrogel ionic circuit based high-intensity iontophoresis device for intraocular macromolecule and nanoparticle delivery. Adv Mater 34(5):e2107315. https://doi.org/10.1002/adma.202107315
165. Bariya M, Nyein HYY, Javey A (2018) Wearable sweat sensors. Nat Electron 1(3):160–171. https://doi.org/10.1038/s41928-018-0043-y
166. Heikenfeld J, Jajack A, Feldman B et al (2019) Accessing analytes in biofluids for peripheral biochemical monitoring. Nat Biotechnol 37(4):407–419. https://doi.org/10.1038/s41587-019-0040-3
167. Kim J, Campbell AS, de Avila BE et al (2019) Wearable biosensors for healthcare monitoring. Nat Biotechnol 37(4):389–406. https://doi.org/10.1038/s41587-019-0045-y
168. Zhao C, Li X, Wu Q et al (2021) A thread-based wearable sweat nanobiosensor. Biosens Bioelectron 188:113270. https://doi.org/10.1016/j.bios.2021.113270
169. Banerjee H, Suhail M, Ren H (2018) Hydrogel actuators and sensors for biomedical soft robots: brief overview with impending challenges. Biomimetics 3(3):15. https://doi.org/10.3390/biomimetics3030015
170. Liu X, Liu J, Lin S et al (2020) Hydrogel machines. Mater Today 36:102–124. https://doi.org/10.1016/j.mattod.2019.12.026
171. Liu J, Zhang X, Liu Y et al (2020) Intrinsically stretchable electrode array enabled in vivo electrophysiological mapping of atrial fibrillation at cellular resolution. Proc Natl Acad Sci USA 117(26):14769–14778. https://doi.org/10.1073/pnas.2000207117
172. Zhang S, Ling H, Chen Y et al (2019) Hydrogel-enabled transfer-printing of conducting polymer films for soft organic bioelectronics. Adv Funct Mater 30(6):1906016. https://doi.org/10.1002/adfm.201906016
173. Wu J, Wu ZX, Xu HH et al (2019) An intrinsically stretchable humidity sensor based on anti-drying, self-healing and transparent organohydrogels. Mater Horiz 6(3):595–603. https://doi.org/10.1039/c8mh01160e
174. Elsherif M, Hassan MU, Yetisen AK et al (2018) Wearable contact lens biosensors for continuous glucose monitoring using smartphones. ACS Nano 12(6):5452–5462. https://doi.org/10.1021/acsnano.8b00829
175. Ying B, Wu Q, Li J et al (2020) An ambient-stable and stretchable ionic skin with multimodal sensation. Mater Horiz 7(2):477–488. https://doi.org/10.1039/c9mh00715f
176. Yu JC, Wang JQ, Zhang YQ et al (2020) Glucose-responsive insulin patch for the regulation of blood glucose in mice and minipigs. Nat Biomed Eng 4(5):499–506. https://doi.org/10.1038/s41551-019-0508-y