Water-Resistant Conductive gels toward Underwater Wearable Sensing

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Abstract: Conductive gels have been developing vigorously as superior wearable sensing materials due to their intrinsic conductivity, softness, stretchability and biocompatibility, showing a great potential in many aspects of our lives. However, compared to their wide application on land, it is significant yet rather challenging for traditional conductive gels to realize sensing application under water. The swelling of gels and the loss of conductive components in the aqueous environment, resulted from the diffusion across the interface, lead to structural instability and sensing performance decline. Fortunately, great efforts have been devoted to improving the water resistance of conductive gels and employing them in the field of underwater wearable sensing in recent years, and some exciting

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achievements have been obtained, which are of great significance for promoting the safety and efficiency of underwater activities. However, there has been no review to thoroughly summarize the underwater sensing application of conductive gels. This review presents a brief overview of the representative design strategies for developing water-resistant conductive gels and their diversified applications in the underwater sensing field as wearable sensors. Finally, the ongoing challenges for further developing water-resistant conductive gels for underwater wearable sensing are also discussed along with recommendations for the future.

1. Introduction

Wearable sensors have attracted tremendous attention and experienced a period of booming development with the advent of the Internet of Things era.[1-3] Through capturing changes in human body and converting them into identifiable electrical signals, wearable sensors can continuously monitor the movement behavior and physiological signals of wearers in a non-invasive manner, which is of great value in many aspects of our lives, especially in personalized real-time healthcare.[4] Compared with traditional wearable sensing devices based on rigid materials, skin-like wearable sensors based on flexible sensing materials enable the conformal integration onto the soft and dynamical skin due to their favorable flexibility and adaptability.[5] This conformal integration without gap between sensors and skin can effectively improve the sensitivity of wearable sensors, and monitor the subtle changes of human body more accurately. Among various flexible sensing materials, such as flexible metals[6-7], conductive polymers[8-9] and carbon materials[10-11], conductive gels are deemed as one of the most promising candidates for wearable sensors owing to their excellent physico-chemical properties in softness, stretchability, transparency, adhesion, self-healability and color-changing capacity[12-14] (Figure 1).

Gels are semi-solid soft materials containing 3D cross-linked polymer networks and a large amount of mobile liquids. The transport of electrons or ions within conductive gels that incorporating conductive materials (e.g., conductive polymers, carbon-based materials, salts, liquid metals, MXenes, etc.) into gel matrices endows gels with shape-dependent and temperature-dependent electrical conductivity, which provide the basis for sensing functions.[15-20] Furthermore, the good biocompatibility and matched mechanical properties of conductive gels endow wearable sensing application with ideal machine-tissue interfaces.[21-22] Nowadays, wearable sensors based on flexible conductive gels have been widely applied in many fields, such as motion monitoring, health management, voice and expression recognition, human-computer interaction.[23-27]

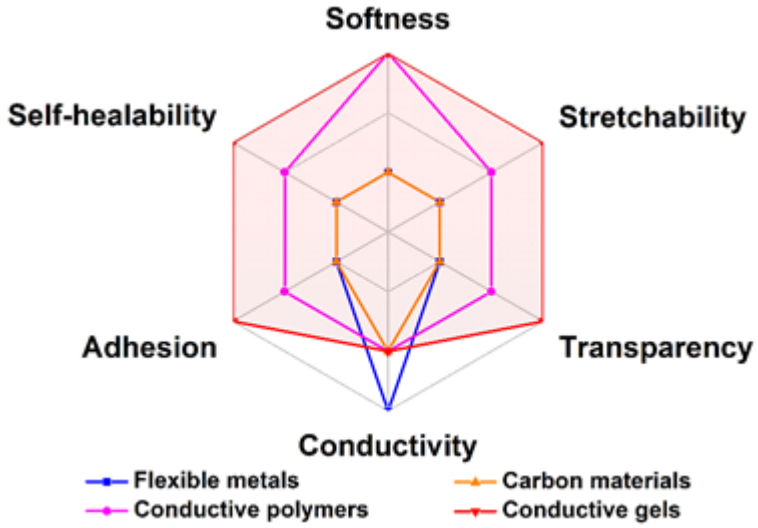

Figure 1. General characteristics of the flexible sensing materials.

With the increase in population attending swimming and diving for underwater exploration or underwater recreation, there is also a growing need to develop the underwater sensing technology, which plays an important role in ensuring the safety of underwater activities.[28] However, although

conductive gel-based wearable sensors have made gratifying progress in the land environment, it is crucial yet rather challenging to realize their application in underwater environment due to the instability of conductive gels in the aquatic environment. Firstly, because of the numerous hydrophilic groups of polymer backbone, conventional gels can imbibe plenty of water accompanied by volume expansion (i.e. swelling), resulting in the loss of the initial network structure and mechanical properties. The swollen gels are usually brittle, and lose the original flexibility and stretchability.[29] Besides, due to the presence of concentration gradients, there is an uncontrollable leakage of conductive component (including conductive ions and nanoparticles) through cross-interface diffusion when the conductive gels are in the underwater environment, which finally lead to the decline of electrical and sensing performance.[30] Moreover, one other issue to note is that the hydration layer formed on the surface of hydrophilic materials prevents molecular-level bridging and interaction between the conductive gels and the substrate, reducing the adhesion strength and wearability of conductive gels.[31] The great difference between the aquatic environment and the land environment seriously prevents wearable sensors based on traditional conductive gels from being applied in underwater sensing.

Over the past few years, water-resistant conductive gels suitable for underwater environments have become a new and burgeoning research field, and some preliminary achievements have been obtained after extensively investigated. For example, some effective strategies, such as packaging architecture, hydrophobic network, and multiple interactions, are developed to realize the structural and functional stability of water-resistant conductive gels in the underwater environment, taking exciting opportunities for underwater wearable sensing. Regrettably, lack of related review has severely limited the further development of conductive gels for underwater sensing application. In

this review, we overview the recent progress in water-resistant conductive gels for application in wearable underwater sensing (**Figure 2**). The representative design strategies for improving the underwater stability and mutilfuctional properties of conductive gels critically discussed. Besides, various underwater wearable sensing applications of water-resistant conductive gels are summarized in detail. Some ongoing research prospects and challenges are proposed to propel the rapid development of this area.

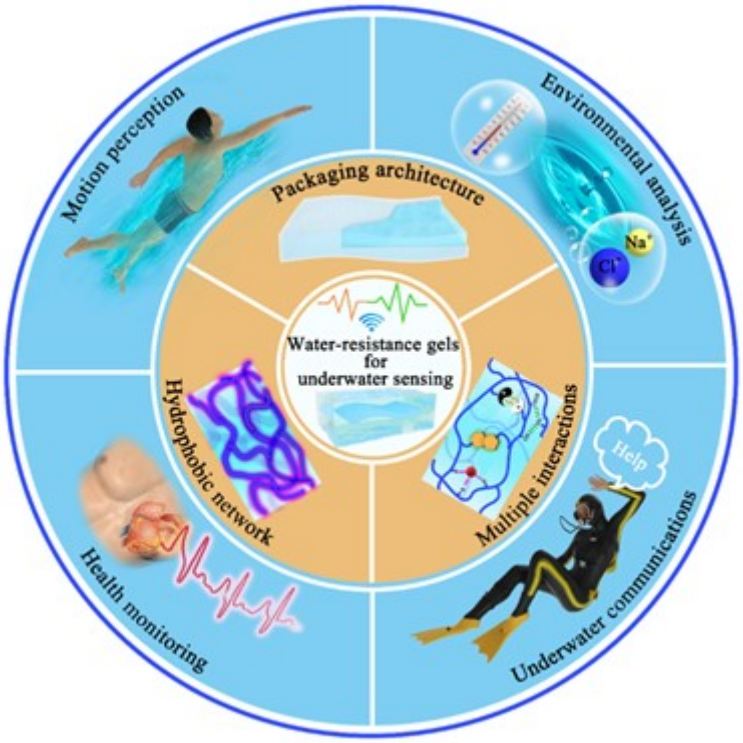

Figure 2. Illustration of general water-resistance strategies of conductive gels (including packaging architecture, hydrophobic network, and multiple interactions) and their applications for underwater sensing, such as motion perception, health monitoring, underwater communications and environmental analysis.

2. Design strategies for water-resistance conductive gels

2.1. Packaging architecture

The direct contact between conductive gels and water, resulting in the uncontrollable diffusion of small molecules (including water molecule, conductive ions and nanoparticles) across the interface to balance the osmotic pressure, is the main reason for the instability of conductive gels in the aquatic environment. Therefore, isolating the contact between gels and water environment by encapsulating conductive gels with additional waterproof film is the simplest way to obtain underwater-stable conductive gels and achieve their underwater sensing applications.

Elastomer, such as silicone, rubber, polyurethane, acrylic elastomer and polydimethylsiloxane, are commonly used as waterproof materials due to their inherently water insensitiveness, flexibility, elasticity, and electric insulativity. The extremely high cohesion and dense network of elastomer can effectively prevent the penetration of small molecules (including water molecules, conductive ions, and other nano fillers), so the waterproof elastomer as encapsulation layer can completely isolate the conductive gels from the surrounding. Since minimizing the exchange of substances between conductive gels and environment, the conductive gels that is physically isolated by the elastomer encapsulation layer possess stable structure and physico-chemical properties.[32] Therefore, packaging with waterproof elastomer layer can protect the conductive gels from water damage effectively in the aquatic environment, leading to a long-term underwater stability in mechanical and electrical properties.[33-34] For example, Ma *et al.* fabricated a multifunctional wearable sensor through sandwiching and encapsulating an ionogel sensing layer (MIS layer) between two acrylic elastomer (VHB) protective layers (**Figure 3a**).[33] Both in the air environment and underwater environment, the multifunctional wearable sensor exhibited good sensing performances with different sensing modes owing to the hydrophobic protection function of VHB. The wearable sensor

based on package structure and biomimetic micronanostructure features prominent sensing performance, such as ultralow detection limit (0.1% strain and 0.001 kPa pressure) and long-term durability and reliability (over 10000 uninterrupted strain or compression cycles). The electrical properties change relied on deformation of conductive gels is one of the important mechanisms to enable strain sensing. The unstable interface between the sensing layer and the protective layer due to the lack of binding force will cause the unexpected slip under deformation process, resulting in interference to the sensing signal. Thus, the robust gel-waterproofing adhesion based on strong interface interactions is critical to realize the structural integrity, synergetic deformation and accurate perception of the packaged sensors. Covalent crosslinking is considered as an effective strategy to form hydrogel-elastomer hybrids with robust interfaces.[35] There are two well-established methods for forming covalent crosslinking between elastomers and hydrogels, including surface initiation method and surface bridge method.[36] For surface initiation method, the hydrophobic initiator (e.g. benzophenone, benzoyl peroxide) can diffuse into the surface of elastomer with the help of organic solvent, and the initiator absorbed in the elastomer play as grafting agent and oxygen scavenger simultaneously to alleviate oxygen inhibition effect and bond the polymers of the hydrogel and elastomer.[35] For example, the benzophenone molecule can abstract a hydrogen from elastomer and generate a free radical to bond the polymer networks of elastomer and hydrogel. Utilizing modified benzophenone strategy, Wang *et al.* prepared an elastomer coated hydrogel optical fiber with hybrid core-cladding structure and robust interface adhesion for versatile underwater sensing (Figure 3b).[37] Benzophenone succeeded in realizing the covalent bonding between elastomer layer and hydrogel sensing layer, contributing to the stability of the tightly adhered hydrogel-elastomer interface under various deformation. Owing to the

cladding of elastomer, the water-proof hybrid fiber is capable to perceive a variety of hydrodynamic stimuli signals in underwater medium of acidic, alkaline, and saline water via structural deformations or transformations. In principle, the surface initiation method is generally applicable to various types of commonly used elastomers, especially with the help of surface treatment technology (e.g., plasma treatment, corona treatment, and acid etching). The surface bridge method uses a bridge molecule (e.g. silanes, silane coupling agents) containing two reaction ends to covalently bond the hydrogel and elastomer separately.[38] Although there have been no reports of water-resistant conductive hydrogels constructed by surface bridge method, it is still a potentially viable option.

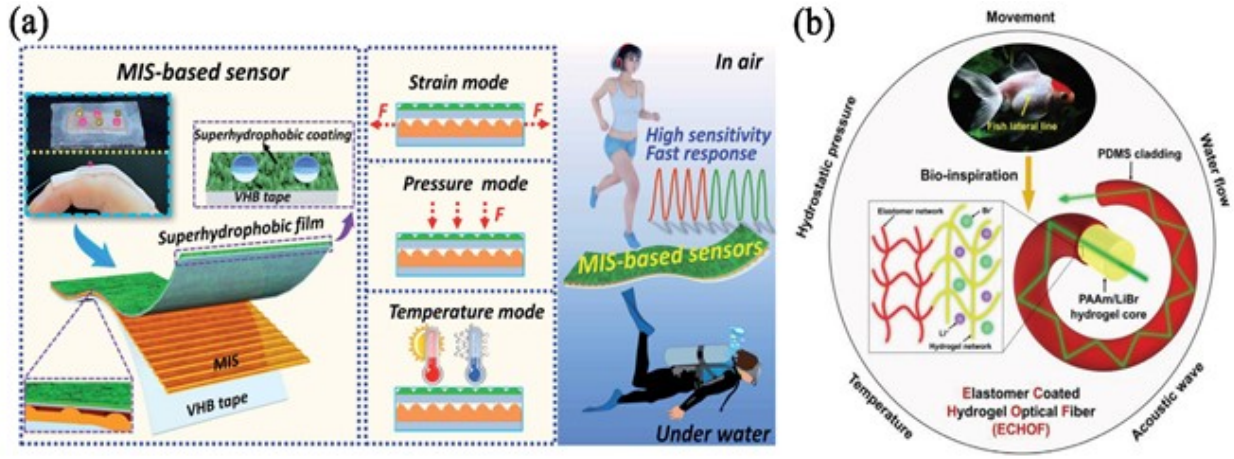

Figure 3. Packaging architecture based on elastomer. (a) Packaging structure and sensing applications of MIS-based multifunctional sensor. Reproduced with permission.[33] Copyright 2021 The Royal Society of Chemistry. (b) Core-cladding structure of elastomer coated hydrogel optical fiber. Reproduced with permission.[37] Copyright 2020 John Wiley & Sons.

Although the elastomer layer can effectively improve the structural and functional stability of conductive gels under water, the high modulus and low tensile strain of elastomers limit the stretchability of wearable sensors, which weaken the sensing performance to a certain extent.

Besides, there are further concerns about the wearable comfort of the sensor and the reliability of sensing weak signals (e.g., pulse, heartbeat) because of the lack of adhesion between the elastomer packaging material and human body. Hydrophobic packaging materials with low modulus, high tensile and underwater adhesion are desired. Compared with traditional packaging materials, polymer gels have aroused researcher's great interest owing to their advantages in the tunable physico-chemical properties and the similar structure to sensing layer. In consideration of the hydrophobicity and swell repellency of organogels, conductive hydrogels and organogels are expected to be integrated to provide excellent sensing performance and water resistance. Introducing double bonds onto the surface of hydrogel as anchoring points for organogel copolymerization is a useful method for fabricating hydrogel–organogel hybrids.[39] Recently, Wang *et al.* developed a full-gel based underwater wearable sensor with tightly-bonded interface by encapsulating the conductive hydrogel with a hydrophobic lipid gel layer (**Figure 4a**).[40] The unsaturated double bonds was grafted on the surface of conductive hydrogel through the reaction between hydroxyl groups and acryloyl chloride, and the hydrophobic lipid gel was synthesized by in-situ copolymerization. Owing to the hydraulic coiling of hydrophobic alkyl chains, the lipid gel reaches a large water contact angle of 137.4° ± 4.9° after soaking in water for 24 h. The good hydrophobic performance and matched mechanical properties of the lipid gel give the wearable sensor excellent waterproof effect and excellent elongation (> 1300%) (Figure 4b and c). Furthermore, the lipid gel can adhere to most substrates in the underwater environment due to hydrophobic interactions, dipole-dipole interactions and hydrogen bonds (Figure 4d). Obviously, thanks to the rich functional groups of the hydrophobic gel, packaging architecture with hydrophobic gel layer is conducive to design multi-functional underwater gel sensors, including high tensile,

underwater adhesion, and even underwater self-healing. Besides, the skin-like modulus enables underwater gel sensors to match the elastic changes in the skin, thus facilitating the monitoring of human signals. The hydrophobic gels need to be further improved in water resistance compared with elastomer, but they still have significant potential applications as waterproof encapsulation materials for underwater sensing gels.

The packaging architecture based on waterproof materials can maintain underwater stability by isolating conductive gels from water environment, which blocking the mass transfer pathway between the conductive gels and surrounding. Packaging architecture can transform almost all traditional gel sensors into underwater sensors and expand the application environment of gel based strain sensors. However, the existence of packaging layer hinders the direct contact between sensing layer and surroundings, limiting the practical application areas of underwater gel sensors, especially in environmental analysis. Therefore, the impact of the packaging layer on the dimensions, sensitivity, and sensing modes (especially the non-strain sensing modes based on contact with conductive gels) of wearable sensors is also of concern in the future.

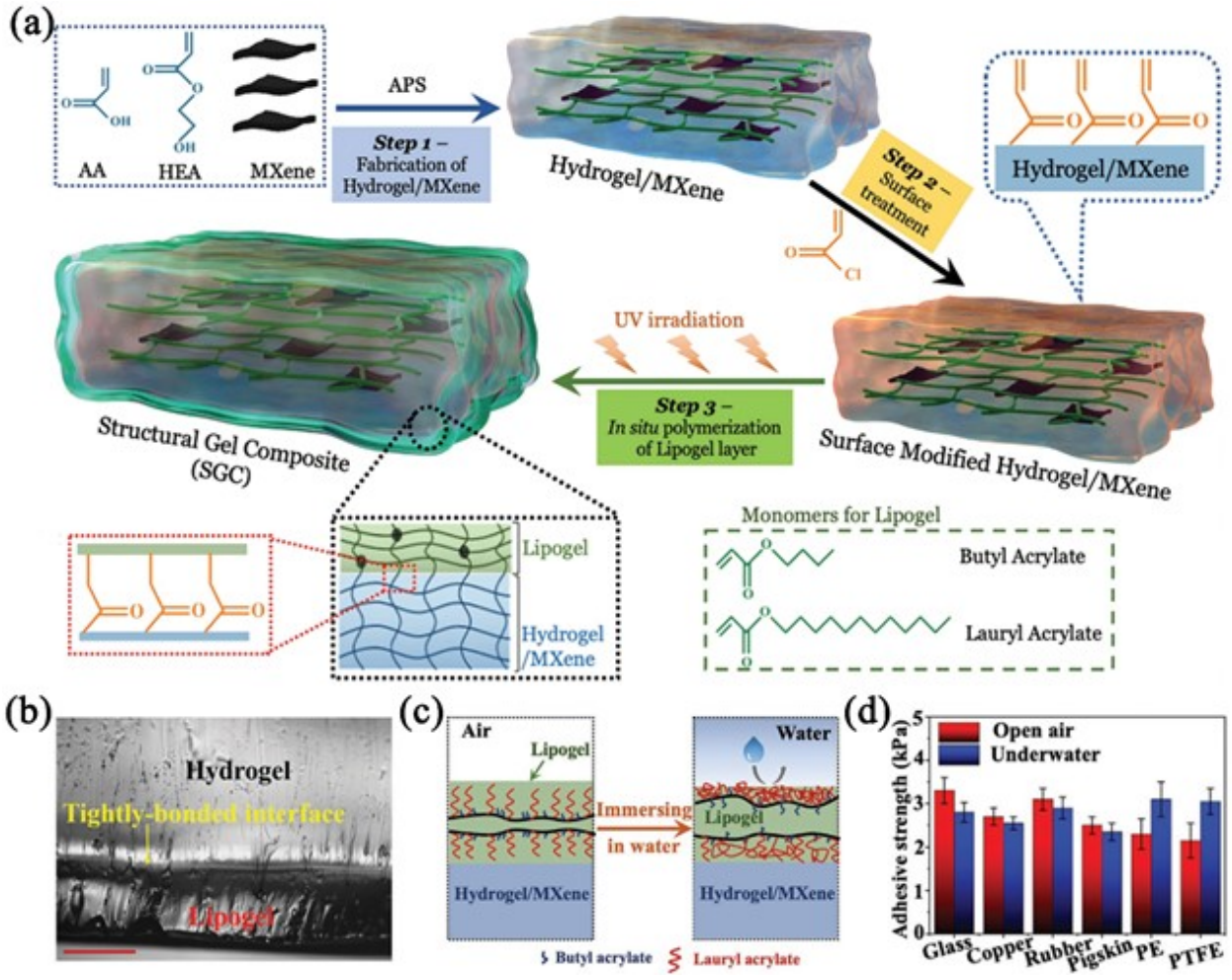

Figure 4. Packaging architecture based on hydrophobic gel layer. (a) Fabrication of full-gel based wearable sensor encapsulated with lipid gel. (b) Optical microscopic images on the cross-section of full-gel based wearable sensor. Scale bar: 100 μm. (c) Schematic illustration of hydrophobic chains accumulation after immersing in water. (d) Adhesive strength of full-gel based wearable sensor on various substrates. Reproduced with permission.[40] Copyright 2022 John Wiley & Sons.

2.2. Hydrophobic network

Most traditional gels, including hydrogels, organogels and ionogels, are composed of hydrophilic polymers and liquids, and the hydrophilicity of the polymer network is an essential reason for the

swelling behavior of gel materials. The strong interaction between water molecules and hydrophilic polymers will compete with the interaction force between polymer chains, thereby weakening the interaction force between polymer chains, which provide the opportunity for water molecules penetrating into the gel. Inspired by this, researchers proposed to construct hydrophobic gels with hydrophobic polymer network, so as to inhibit the swelling behavior of gels in the aquatic environment and improve the structural and functional stability of conductive gels for underwater application.

Due to the hydrophilic polymers' affinity to water, the hydrophilic conductive gels are susceptible to free diffusion and exchange of water molecules across the gel surface in the aquatic environment, resulting in the direct penetration of water and subsequent swelling behavior of gels. On the contrary, the incompatibility of the hydrophobic polymer with water can significantly suppress the substance diffusion process, acting as a diffusion barrier. Therefore, the hydrophobic surface of conductive gel constructed by hydrophobic polymers can terminate most of the molecular transport across the boundaries of the conductive gel, because the hydrophobic surface separate the interior domain of gel and the outside water environment.[41] As a result, hydrophobic polymer networks will indeed effectively improve the anti-swelling capacity and underwater stability of conductive gels by inhibiting the interfacial diffusion of water molecules and substances (such as ions) dissolved in water.

Ion conduction based on directional migration within gels is one of the most common conductive mechanisms of sensing gels, and it is essential to inhibit ion diffusion across the interface to achieve electrical stability of ion-conducting gels under water, because the loss of conductive components is another important reason for the deterioration and even lost of gel sensing performance in the

aquatic environment. On this purpose, hydrophobic ionic liquids, such as 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([EMIm][TFSI]), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide ([BMIm][TFSI]), butyltrimethylammonium bis(trifluoromethanesulfonyl) imide ($[N_{4111}][TFSI]$), methyltributylammonium bis(trifluoromethanesulfonyl) imide ($[N_{1444}][TFSI]$), are usually used as conductive component of ion-conducting gels owing to their incompatibility with water.[42-49] Utilizing the chemical compatibility between highly polar fluoro-polymer PVDF-co-HFP and fluorine-rich ionic liquid [EMIm][TFSI], Cao *et al.* prepared a submersible electronic skin sensors based on ionogel (named as GLASSES) by physical crosslinking strategy (**Figure 5a**).[42] The abundant carbon-fluorine (C–F) bonds enable ionogel to weakly interact with water molecules because the C–F bonds very poor hydrogen donors and acceptors. As a result, the fluorine-rich structures of polymer and ionic liquid enhance their hydrophobicity, and minimize the perturbation from the aquatic circumstance. Besides, the highly reversible ion-dipole interactions between polymer and ionic liquid endow ionogel with self-healing function, even in various aqueous environments (Figure 5b). Recently, a similar underwater ionic skin (PUF-IL) prepared by blending [EMIm][TFSI] with fluorinated polyurethane elastomer (PUF) was further investigated by Liu's group (Figure 5c).[43] The abundant and strong fluorine-cation interactions in PUF-IL ionogel were verified through computational chemistry and extensive spectroscopy analysis (Figure 5d). Due to the cations caught by fluorine-rich segments, the ionic conductivity of PUF-IL can keep stable in a 7-days continuous underwater test. Of far greater significance, the fluorine-cation interaction not only improve the ionic conductivity of PUF-IL ionogel by generating more freedom ion, but also suppress the exchange or leak out of ions under aquatic circumstances, leading to stable electrical and sensing properties in water or even ultrasonication.

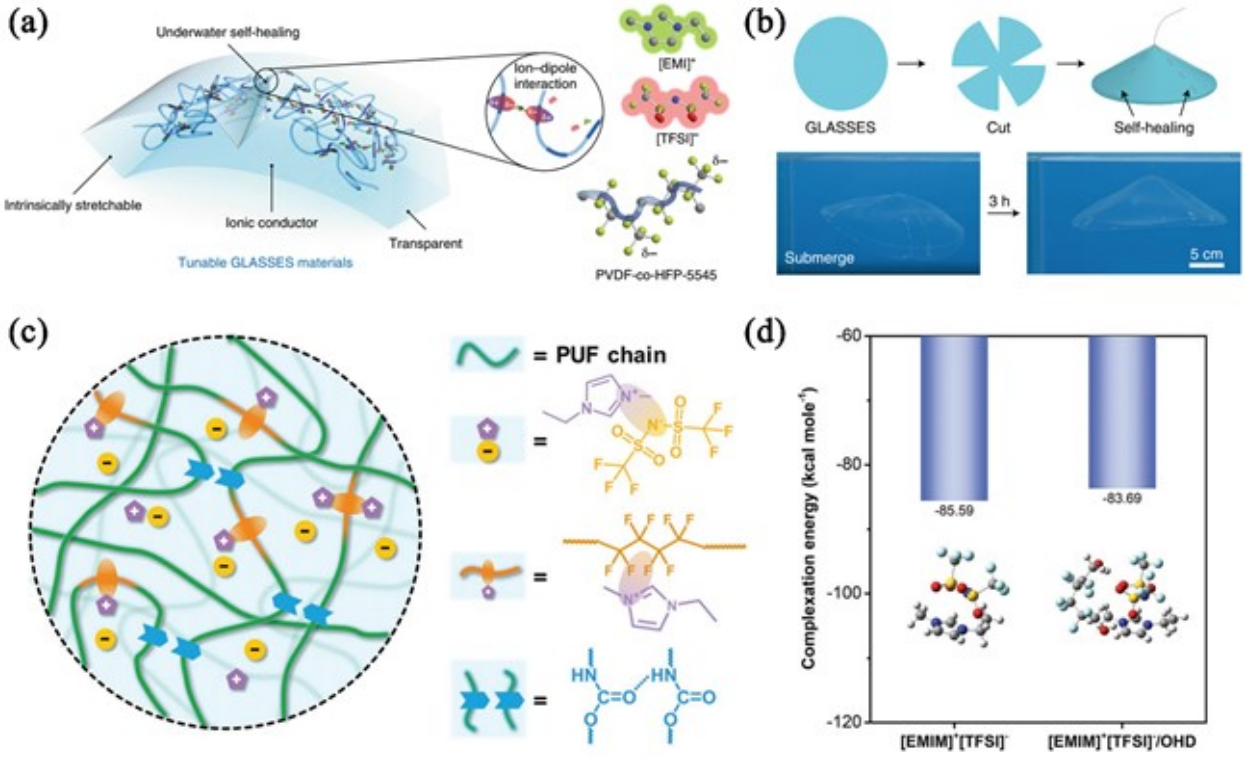

Figure 5. Hydrophobic ionogel by physical mixing of fluoro-polymer and ionic liquid. (a) Submersible self-healing electronic skin (GLASSES) based on PVDF-co-HFP and ionic liquid. (b) Self-healing ability of GLASSES in water. Reproduced with permission.[42] Copyright 2019 Springer Nature. (c) Electric interactions, fluorine-cation interactions and hydrogen bonds between the components of underwater ionic skin PUF-IL. (d) Complexation energy of PUF-IL via computational chemistry. Reproduced with permission.[43] Copyright 2022 John Wiley & Sons.

Compared with the simple physical mixing of hydrophobic polymer and ionic liquid, diverse hydrophobic network of gels can be designed by the free radical in-situ polymerization of hydrophobic monomer in ionic liquid, which is beneficial to improve the performances of conductive gel and achieve multifunction of sensor. Utilizing one-step polymerization of hydrophobic *tert*-butyl acrylate in hydrophobic [BMIm][TFSI], we developed a fully hydrophobic ionogel with an excellent water-resistance ability, long-term underwater stability and robust underwater adhesion.[50] The

dynamic hydrophobic interface based on hydrophobic functional groups self-assembly and hydrophobic aggregation can suppress the diffusion of molecules effectively (**Figure 6a**), ensuring the sensing performance of our ionogel sensor is stable and consistent even after 5 months of soaking treatment (Figure 6b). Other ionogels with specific functions can also be achieved by the polymerization of one or more functional monomers, such as high conductivity, recyclability, ultrastretchability, solvent and temperature resistance, underwater self-healing ability and underwater adhesiveness.[44-45, 51] By virtue of the similar structure to fluorine-rich solvent ionic liquid, the polymerizable ionic liquids with double bonds are often used as monomer to prepare the expected hydrophobic ionogel based wearable sensors.[47-49, 52] For example, Yu *et al.* designed a submersible soft sensor based on hydrophobic ionogel by one-step polymerization of fluorine-rich ionic liquid monomer in another fluorine-rich ionic liquid (Figure 6c).[47] The high miscibility of the resulting poly(ionic liquid) with the solvent ionic liquid endows the ionogel sensors with high transparency in the aquatic environment. Furthermore, various interactions (including ion–dipole, ion–ion, dipole-dipole interactions) rooted from the hydrophobic dynamic networks with abundant functional groups in the ionogel enable ionogel sensor mechanical-adjustable, underwater self-healable, underwater adhesive and 3D printable. Hydrophobic ionogels based on hydrophobic network are usually characterized by ultra-high stretch, high-linear signals and transparency due to the ion-conducting mode, but the sensing sensitivity is low and the conductive ions are easily lost.

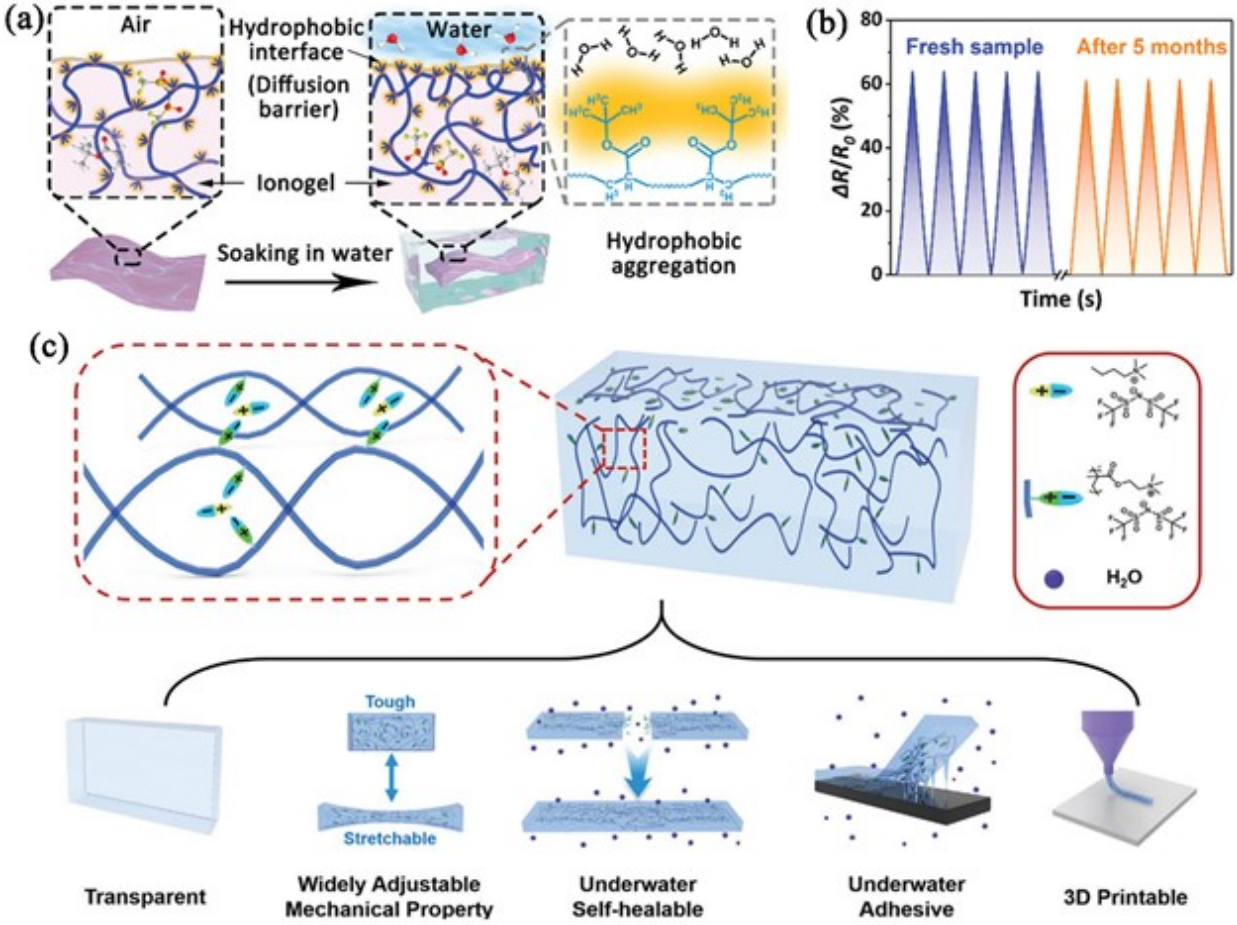

Figure 6. Hydrophobic ionogels by in-situ polymerization of hydrophobic monomer in ionic liquid. (a) Hydrophobic aggregation effect of the fully hydrophobic ionogel sensor after soaking treatment. (b) Relative resistance comparison of the fully hydrophobic ionogel sensor before and after soaking for 5 months. Reproduced with permission.[50] Copyright 2021 The Royal Society of Chemistry. (c) Structure and wide spectrum mechanical properties of underwater ionogel sensor. Reproduced with permission.[47] Copyright 2021 John Wiley & Sons.

Electron conduction based on electron migration is another important conductive mechanism for realizing sensing function. Generally, the electron-conducting gels can be fabricated by doping conductive nano fillers (e.g., nano metal, carbon nanotube, graphene, MXenes) or mixing conductive

polymers (e.g., polyaniline, polypyrrole, polythiophene) into the gel system.[53] Compared to conducting ions, the conductive nano fillers and conductive polymers have lower solubility and diffusion in water, so the loss of conductive components of gels is slight or even negligible when the conductive gels are immersed in the aquatic environment. Therefore, the water-resistant electron-conducting gels consists of conductive nano fillers and conductive polymers have been widely studied, and some underwater gel sensors have been developed on this basis.[54-56] Benefitting from the intrinsic hydrophobic properties and the good electroconductibility of polyaniline (PANI), Chen *et al.* constructed a hydrophobic nanostructured conductive hydrogel fiber based water resistant sensor by growing secondary PANI polymer chains inside the initial hydrophobic nanocomposite gel (NC gel) matrix (**Figure 7a**).[54] The heterogeneous networks and multimolecular interaction between polymer chains hold the stability of network structure enhance the tensile mechanical properties of hydrogel sensor. By introducing graphene into hydrophobic methacrylamide hydrogel, a water-insensitive hydrogel sensor was successfully fabricated, and the hydrophobic interaction, hydrogen bonding, and chain diffusion of the hydrophobic supramolecular network empower underwater self-healing ability for hydrogel sensor in the aquatic environment (Figure 7b).[56] Although electron-conducting hydrophobic gels possess higher sensing sensitivity compared to ion-conducting gels due to the high conductivity and the sensing mechanism based on contact resistance effect, but they are usually opaque and have poor linearity in sensing signals.

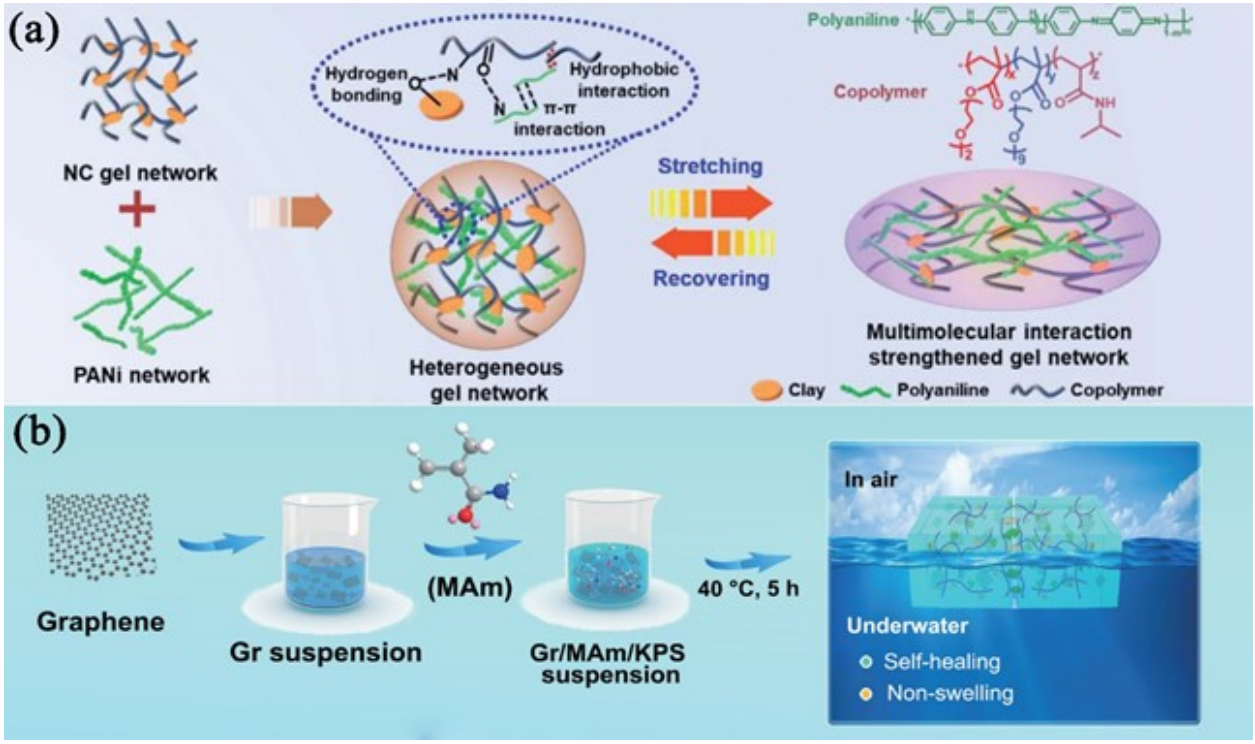

Figure 7. Electron-conducting hydrophobic gels. (a) Heterogeneous networks and multimolecular interaction for PANI/NC hybrid gel sensor. Reproduced with permission.[54] Copyright 2021 The Royal Society of Chemistry. (b) Underwater flexible electronic skin based on underwater self-healing and anti-swelling hydrogels containing graphene. Reproduced with permission.[56] Copyright 2021 Copyright 2019 Springer Nature.

The construction of hydrophobic network can effectively reduce the hydrophilicity of conductive gels and inhibit their swelling behavior in the underwater environment, leading to a higher network stability for underwater application. Meanwhile, the hydrophobicity of polymer network could effectively repel water molecules and generate the hydrophobic interaction between gel sensors and different substrates (including body and gels), which is conducive to achieving underwater adhesiveness and underwater self-healing ability. Furthermore, the hydrophobic network strategy does not have an isolation layer similar to the packaging architecture strategy, so it can be used in a

variety of sensing applications, including motion perception, health monitoring and environmental analysis. However, hydrophobic performance of the existing conductive gels is still not perfect, their water contact angle is below 130 °. The superhydrophobic conductive gels with better water resistance remain to be explored in the field of underwater sensing.

2.3. Multiple interactions

During the swelling process of gels, the extension of the network chains leads to a crosslinking density-dependent elastic retractive force, which is an opposite and restraining force to swell. As a result, the gels' swelling capacity depends on the balance between the swelling force (including polymer-water interaction force, electrostatic repulsion force, osmotic force) and the elastic retractive force.[29] According to the swelling equilibrium equation derived from the thermodynamic theory, the crosslinking density, as well as the hydrophilicity of polymers, is one of important parameters affecting the swelling capacity of gels. Generally, higher crosslinking density means fewer number of segments between two successive crosslinks in the network, which leads to lower deformability of polymer network. Furthermore, the high crosslinking density increases the elastic retractive force of network, and further restrains the elongation of network chains. Based on the above mechanism, increasing the crosslinking density can effectively inhibit the swelling behavior of gels, which is expected to achieve anti-swelling capacity. Therefore, the strategy that designing multiple crosslinking interactions (e.g. covalent bond, hydrogen bond, electrostatic interaction, hydrophobic association, metal coordination, etc.) between polymer chains, that can improve the

crosslinking density of gels and inhibit their swelling behavior in water, has attracted wide attention in the area of water-resistant conductive gels.

Too many covalent crosslinking joints by small molecular crosslinkers will reduce the tensile property of gels, which is not conducive to sensing application. On the contrary, the non-covalent crosslinking network based on non-covalent interactions can not only inhibit swelling, but also improve mechanical properties and even give the gel based wearable sensor desirable functionality, such as self-healing, adhesiveness and so forth. Introducing diversified functional groups, such as charged group and hydrophobic group, into gels through the copolymerization of different monomers is an effective method to obtain anti-swelling gels with multiple non-covalent crosslinking interactions.[57-60] With the assistance of cationic surfactant cetyltrimethylammonium bromide (CTAB), Qi *et al.* developed an anti-swelling conductive hydrogel for underwater sensing application by free-radical copolymerization of hydrophilic acrylic acid (AA) and hydrophobic lauryl methacrylate (LMA) (**Figure 8a**).[57] The hydrophobic association between nonpolar hydrophobic tails of CTAB and the hydrophobic segments of LMA acts as physical crosslinking sites of the hydrogel network, and the strong electrostatic interaction between positively charged headgroup of CTAB and negatively charged carboxy groups of PAA further increases the crosslinking density of hydrogel. The multiple interactions endow conductive hydrogel with outstanding anti-swelling capability (>15 days) and robust wet adhesion to diverse materials (Figure 8b), ensuring the underwater sensing stability of the P(AA-*co*-LMA)$_{CTAB}$ hydrogel sensors. Besides, the synergistic hydrophobic and hydrophilic segments can even make conductive gels both have excellent water resistance and organic solvent resistance through the self-adjustment of the polymer network in diverse liquid media (Figure 8c).[58]

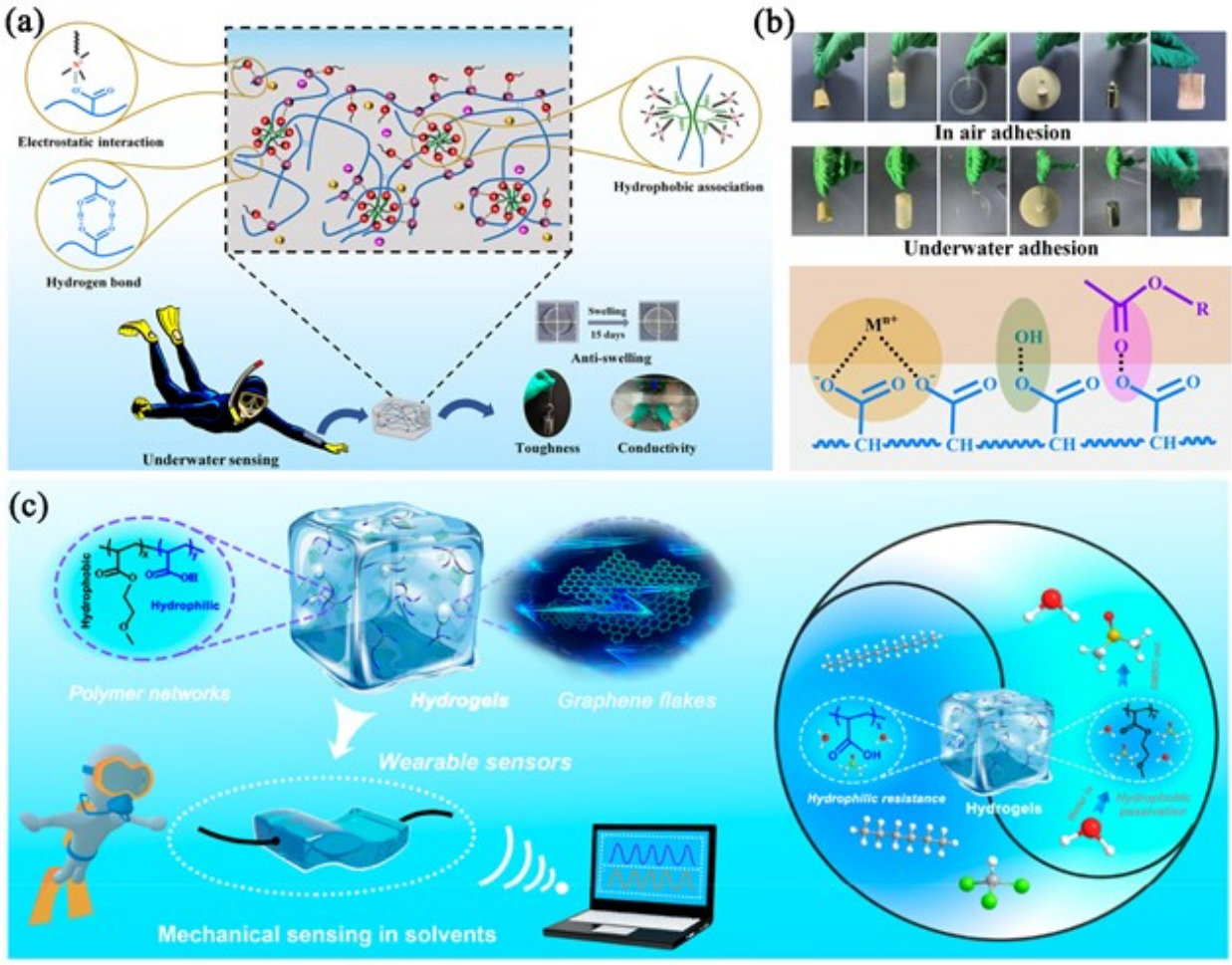

Figure 8. Anti-swelling gels based on electrostatic interaction and hydrophobic association. (a) Electrostatic interaction and hydrophobic association of the anti-swelling P(AA-*co*-LMA)$_{CTAB}$ hydrogel. (b) Adhesive performances of the P(AA-*co*-LMA)$_{CTAB}$ hydrogel under water. Reproduced with permission.[57] Copyright 2022 American Chemical Society. (c) Schematic of the solvent-resistant graphene-assisted hydrogel in diverse solvents. Reproduced with permission.[58] Copyright 2020 American Chemical Society.

In addition to the electrostatic interaction and hydrophobic association, there are many other interactions that increase the crosslinking density and underwater stability of conductive gels, such as metal coordination, chain entanglement, and microcrystalline domains. Through metal

coordination, one metal ions can anchor multiple ligand groups on polymer chains with together to form new crosslinking sites between different polymer chains. Utilizing multiple dynamic reversible bonds, including catechol-Fe^{3+} metal coordination bonds, hydrophobic interactions, electrostatic interactions, and hydrogen bonds, a underwater self-healing, wet-adhesion and anti-swelling conductive hydrogel silk fibroin/ tannic acid @ polypyrrole (SF/TA@PPy) with a tight and uniform gel network was prepared without the use of additional covalent crosslinking agents (**Figure 9a**).[61] The strong cumulative effect of metal coordination bonds and various intermolecular non-covalent interactions stabilizes the network structure of gels under water.[61-64] Chain entanglement refers to the mutual interpenetration of the polymer chains under the collective effect of all surrounding chains, which impose topological constrains on each other and prevent them from moving easily, playing as physical crosslinking joints.[65] Inspired by the topological crosslink of chain entanglement, Zhao *et al.* developed a non-swelling conductive hydrogel poly(acrylic acid-2-methoxyethyl acrylate)-chitosan-Fe^{3+} (named as P(AA-MEA)-CS-Fe) by introducing chitosan (CS) to polymer network (Figure 9b).[66] Due to the synergistic effect of chain entanglement and other multiple interactions, the P(AA-MEA)-CS-Fe hydrogel exhibits enhanced swelling resistance and stable strain sensitivity in extensive aqueous solutions, physiological saline, and seawater, even after immersing in water for 7 days. The formation of microcrystalline domains of polyvinyl alcohol (PVA) macromolecules at low temperature is one of the keys to preparing PVA hydrogels by physical crosslinking method. On the basis of the first original network, a double-network structure can be constructed by introducing the PVA network based on microcrystalline domains through freezing/thawing process. Because the two networks of double-network hydrogel interpenetrate each other, the introduction of by PVA network by forming microcrystalline domains is an effective approach to increase the crosslinking

joints between polymer chains and enhance the swelling resistance.[67-68] For example, Ren *et al.* prepared a tough, anti-swellable, and ionic conductive double-network hydrogel with freezing/thawing and HCl treatment (named as DN-FT-HCl), that consisted of PVA network and copolymer network of [2-(methacryloyloxy) ethyl]dimethyl-(3-sulfopropyl) ammonium hydroxide (SBMA) and 2-hydroxyethyl methacrylate (HEMA) (named as P(SBMA-*co*-HEMA)) (Figure 9c).[67] The dense network structure induced by PVA crystallite and the reduced osmotic pressure driven by electrostatic repulsion leads to a low swelling ratio (equilibrium swelling ratio of 9% in 30 days) and a high toughness.

Introducing multiple interactions between different polymer chains can not only significantly improve the crosslinking density and swelling resistance of conductive gels, but also facilitate the realization of underwater adhesion, underwater self-healing and other functions. Similar to hydrophobic network strategy, the multiple interactions strategy is suitable for a variety of underwater sensing applications. However, the high mechanical strength resulted from high crosslinking density will limit the synchronous movement of the underwater gel sensors with skin, and this method has no significant effect on preventing the loss of conductive components from gels, especially the solvated conducting ions. The long-term sensing stability of these multiple interactions based underwater sensing gels in the aquatic environment yet to be investigated and verified.

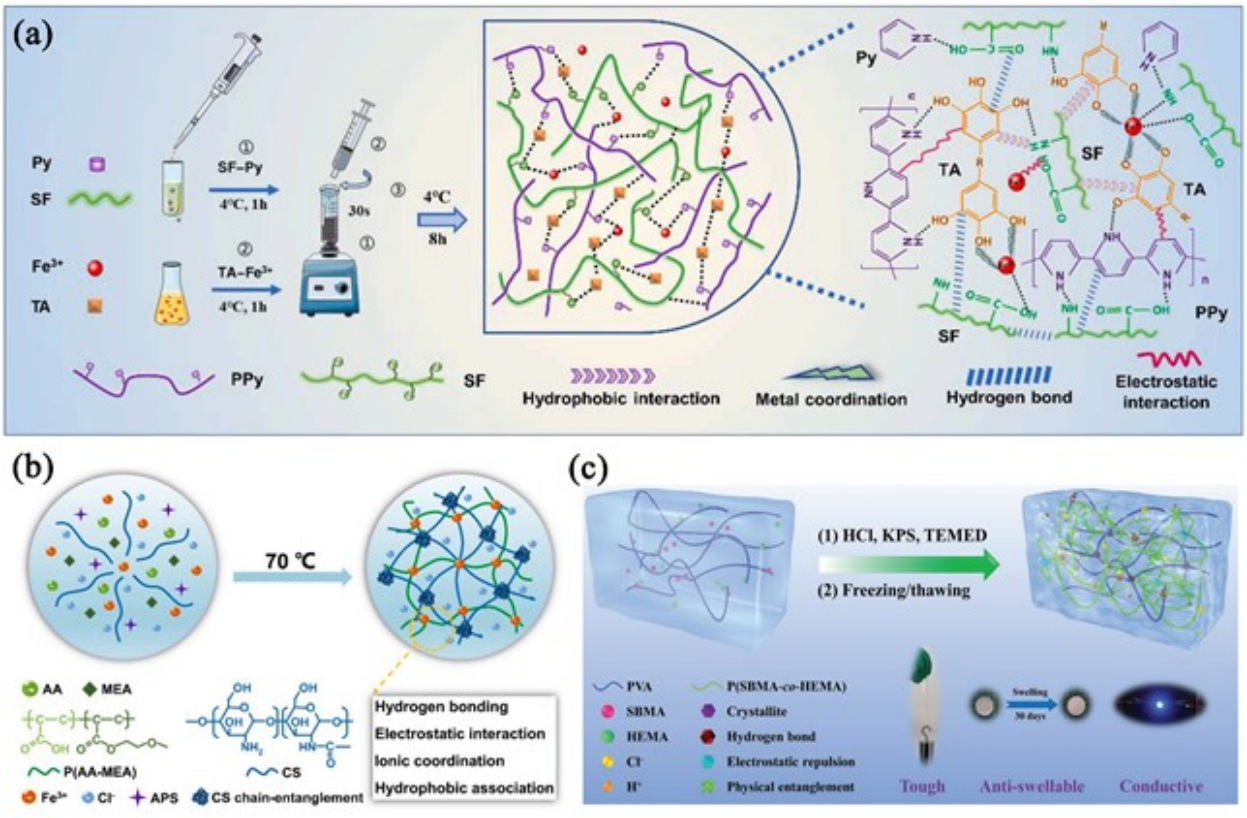

Figure 9. Multiple interactions. (a) Metal coordination of the anti-swelling SF/TA@PPy conductive hydrogel. Reproduced with permission.[61] Copyright 2022 Elsevier. (b) Chain entanglement of the non-swelling P(AA-MEA)-CS-Fe Hydrogel. Reproduced with permission.[66] Copyright 2022 Elsevier. (c) PVA microcrystalline domains and electrostatic repulsion of the anti-swelling DN-FT-HCl hydrogel. Reproduced with permission.[67] Copyright 2021 John Wiley & Sons.

Although three feasible strategies have been proposed to improve the underwater stability of conductive gels, they all have their own advantages and disadvantages in various properties and sensing performance. **Table 1** summarizes the performances of water-resistant gel based underwater wearable sensors that reported previously, which helps to establish an intuitive understanding about the differences between these strategies and provide a guidance for the design of water-resistant conductive gels.

Table 1. Performance comparison of water-resistant gel based underwater wearable sensors.

Design strategy	Components	sensitivity	Limit of detection	Stability	Features	Appliaction	Ref.
Packaging architecture	WPU/[EMIM][TFSI]/ mHNTs-VHB	GF = 1.28 (0.1~100%) GF = 2.31 (100~400%)	0.1% strain and 0.001 kPa pressure	> 10000 cycles	Anti-swelling	Motion perception Health monitoring Underwater communications Environmental analysis	33
	PAA/Ag^0-PE	S = 57 kPa^{-1} (<75 Pa) S = 171.4 kPa^{-1} (75~1500 Pa)	0.075 Pa	> 1500 cycles	Low-Voltage Operation	Environmental analysis	34
	P(AA-co-HEA)-MXene-Lipogel	GF: 4.14~14.51 (0~1000%)	-	> 90 days > 2000 cycles	Anti-swelling Underwater adhesion High-Stretchability	Motion perception Underwater communications tactile trajectory tracking	40
Hydrophobic network	PUF/ [EMIM][TFSI]	-	-	> 7 days	Anti-swelling High transparency	Health monitoring	43
	PHFBA-r-OEGA-[BMIM][TFSI]	GF = 1 (0~200%)	-	> 5000 cycles	Anti-swelling Ultrastretchability Underwater healability High-transparency	Motion perception	45

	PMMA-PIL/ $[N_{4111}][NTf_2]$	GF = 2.3 0.2 °C	-	> 14 days	Anti-swelling Underwater adhesion 3D printability Temperature tolerance	Motion perception Underwater communications Environmental analysis	46
	P[MATAC][TFSI] /$[N_{4111}][TFSI]$	GF: 1.66~ 4.67 (0~1000%)	-	> 10 days > 5000 cycles	Anti-swelling Underwater adhesion Underwater healability High-Transparency 3D printability	Motion perception Underwater communications Environmental analysis	47
	P[VBIm][NTf_2]/ $[N_{1444}][NTf_2]$	GF = 3.4 (0~300%)	< 1%	> 21 days	Anti-swelling Underwater adhesion	Motion perception Health monitoring Underwater communications	49
	P(t-BuA)-[BMIM][TFSI]	GF: 1.30~1.06 (0~400%)	< 5%	> 5 months > 5000 cycles	Anti-swelling Underwater adhesion	Motion perception Underwater communications	50
	P(TFEA-co-AAm)/ [EMIM][TFSI]	GF: 0.83~1.85 (0~600%) S = 5.93 Pa^{-1} (1~10 kPa) S = 2.66 Pa^{-1} (10~100 kPa)	1 kPa	> 24 h > 300 cycles	Anti-swelling Underwater adhesion Underwater healability Recyclability	Motion perception Health monitoring Underwater communications	51
	OA/NIPAM/DMSO/ AIBN/Fe^{3+}	GF = 1.96 (0~70%)	0.45 Pa	3981 cycles	Underwater adhesion	Motion perception Underwater	55

		S = 5.22 kPa^{-1} (<15 kPa) S = 2.82 kPa^{-1} (15~35 kPa)				communications Detecting ultrasound	
	PMAm/Gr	1.96~4.55 (0~50%)	< 0.2%	-	Anti-swelling Underwater healability	Motion perception	56
Multiple interactions	$P(AA\text{-}co\text{-}LMA)_{CTAB}$	0.42~7.39 (0~900%)	-	> 100 cycles	Anti-swelling Underwater adhesion Recyclability	Motion perception	57
	P(MEA-co-AA)/Gr	0.62~3.40 (0~500%)	0.2% strain and 0.7 kPa pressure	> 500 cycles	Anti-swelling Underwater adhesion	Motion perception	58
	P(AN-co-AAm-co-MMA)	GF = 2.08 (0~300%) GF = 8.17 (300~700%)	-	-	Anti-swelling Underwater healability Underwater adhesion	Motion perception Underwater communications	59
	BA-AA-CABIL-TA	-	-	> 350 cycles	Anti-swelling Underwater adhesion	Health monitoring	60
	SF/TA@PPy	GF = 0.72 (0~500%)	-	> 150 cycles	Anti-swelling Underwater healability Underwater adhesion Biocompatibility	Motion perception Underwater communications	61
	CNT@DNHG	-	0.1% strain and	> 50000 cycles	Anti-swelling	Motion perception Environmental	62

		0.26 kPa pressure			analysis	
DCMC/CS/PAA/Al^{3+}	1.75~15.56 (0~800%)	-	-	Underwater healability Underwater adhesion	Motion perception	63
P(DMAEMA-co-HEA)-SDS-C_{18}-Fe^{3+}	0.44	-	> 72 h	Anti-swelling Underwater adhesion	Motion perception	64
P(AA-MEA)-CS-Fe^{3+}	1.60~2.57 (0~400%)	< 1%	> 20 days	Anti-swelling High toughness	Motion perception	66
PVA-P(SBMA-co-HEMA)-HCl	1.43~3.36 (0~300%)	< 1%	> 30 days > 1000 cycles	Anti-swelling High toughness	Motion perception	67

3. Multifunctional properties for underwater sensing gels

The underwater stability (including anti-swelling ability, leakage proof and stable conductivity) achieved by water-resistant design using above strategies is the basic demand for underwater sensing application of conductive gels. Beyond that, it is also imperative to develop underwater gel sensors with additional functions, such as high stretchability, underwater adhesion, underwater self-healability, recyclability, 3D printability, and so on. These multifunctional conductive gels rooted from special material design will greatly improve the processing technology sensing performance and practicability of underwater gel sensors.

The electric property of conductive gel changed synchronously with its size under the action of external force is the main basis of realizing the sensing of strain sensor. Therefore, the sensing range and sensitivity of underwater gel sensors can be affected by the mechanical properties of water-resistant conductive gels, especially the stretchability. High stretchability are desirable to improve the sensing range and sensitivity of gel sensors. Dissipating significant amounts of mechanical energy under large deformation is a general principle for the design of high-stretchable gels. Introducing reversible crosslinking of polymer chains into gels have been widely used to induce mechanical dissipation in tough gels, and it was also working in water-resistant conductive gels. Recently, a highly stretchable and solvent-resistant multifunctional ionogel without chemical cross-linker was reported by Xu *et al.*[51] Owing to the abundant noncovalent interactions (including the hydrogen bonding and the ion–dipole interactions) served as the "temporary crosslinking sites", the multifunctional physical crosslinking ionogel could destroy the reversible bonds and network to dissipate energy when it were subjected to a high tensile strain, leading to a high stretchability (breaking strain of 1089-2066%) and wide sensing range under water (Figure 10a). Similarly, the internal ion-ion and ion-dipole interactions between hydrophobic IL and hydrophobic polymer chains could play as reversible interactions to dissipate energy during the stretching process, which improving the mechanical stretchability of water-resistant ionogel.[47-48] Besides, adding fibers or fillers also can significantly dissipate mechanical energy. For example, Zhao *et al.* prepared a non-swelling double network conductive hydrogel by adding chitosan to first network, and the chitosan-enhanced hydrogel were stretched to 12 times of its original length without any breakage since the sacrificial force (hydrogen bonding and chain-entanglement) provided by chitosan.[66] A similar high-stretchable underwater hydrogel sensor based on polysaccharide doping was reported by Ling *et al.*,

and it exhibited an outstanding sensitivity (GF = 15.56) in the strain range of 530-800%.[63] In addition to stretchability, the mechanical recoverability of gel sensor after strain is one of the important conditions for achieving good sensing performance, especially the stability and repeatability of sensing signal. The introduction of microphase structure (such as microdomain)[69] or dual network structure[70] has been proved to be beneficial to the fast recovery of the deformed gel, so as to realize the rapid response and long-term stability under repeating sensing. These strategies are expected to be introduced into underwater gel sensors.

Underwater adhesion based on underwater interface interactions play an important role in providing a robust and stable interface for electronics and substrate in aquatic environment. Eliminating the hydration layer between underwater sensing gels and substrate is essential to achieve underwater adhesion, because the water molecules will weaken the interface interactions. Designing hydrophobic surface with hydrophobic functional groups is an effective strategy to form a durable and stable underwater adhesion. Inspired by barnacles, He *et al.* developed an underwater adhesion hydrogel (named as MXene/PHMP hydrogel) by copolymerizing hydrophobic monomers (2-phenoxyethyl acrylate and 2-methoxyethyl acrylate) with hydrophilic monomer (N-(2-hydroxyethyl) acrylamide) in dimethylsulfoxide and subsequent solvent replacement.[71] The MXene/PHMP hydrogel exhibited strong adhesion on most substrates under water, which is attributed to the hydrogen bonding interaction and the extra physical interaction (hydrophobic conjugation and π−π conjugation) formed by the introduced hydrophobic groups (methyl and benzene rings) (Figure 10b). The interfacial hydration layer can be effectively penetrated by the hydrophobic groups of MXene/PHMP hydrogel sensor, leading to an excellent sensing signal stability for over 1000 tensile cycles. In addition to the benzene rings, other hydrophobic groups (e.g. long-

chain alkane, hydrophobic anions, etc.) also helps to form underwater adhesion.[47, 50, 57] The water-resistant conductive gel with hydrophobic surface even exhibited strong bonding strength in various aqueous solutions, including seawater, acid solution, and alkali solution.[60] Furthermore, the covalent interactions between water-resistant conductive gel and substrate also enable strong adhesion under water. For example, Niu *et al.* developed an organohydrogel sensor composed of gelatin and poly(acrylic acid-N-hydrosuccinimide ester).[72] A robust underwater interfacial adhesion (~325 J m^{-2}) was observed between organohydrogel and tissue under water, owing to the covalent interactions between N-hydrosuccinimide (NHS) ester and amino groups from tissue by amide bonds, as well as the multiple interactions (including hydrogen bonds and electrostatic interactions).

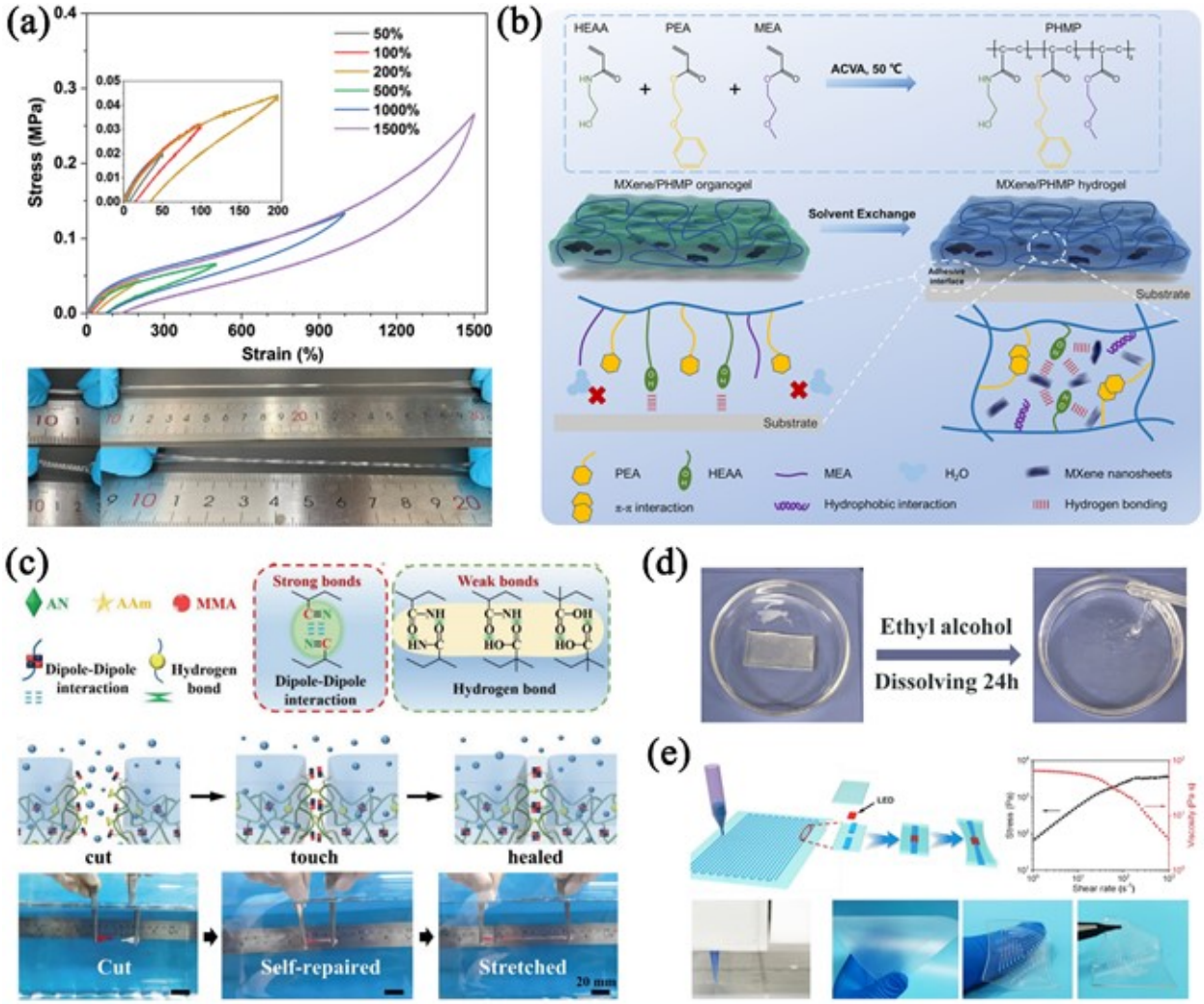

Figure 10. Multifunctional properties. (a) High stretchability of the water-resistant ionogel. Reproduced with permission.[51] Copyright 2021 John Wiley & Sons. (b) Underwater adhesion interactions of adhesive MXene/PHMP hydrogel. Reproduced with permission.[71] Copyright 2022 American Chemical Society. (c) Underwater self-healing interactions of the water-resistant supramolecular hydrogel. Reproduced with permission.[59] Copyright 2022 John Wiley & Sons. (d) Recyclability of the P(AA-co-LMA)$_{CTAB}$ Supramolecular hydrogel sensor. Reproduced with permission.[57] Copyright 2022 American Chemical Society. (e) Shear-thinning behavior and 3D printability of the ionogel. Reproduced with permission.[47] Copyright 2021 John Wiley & Sons.

When subjected to the overload of external force in complex operation environment, underwater gel sensors are prone to damage, which affects the accuracy of sensing signal and misleads the subsequent data analysis. Developing water-resistant conductive gels that can self-heal in aqueous environment could improve the stability and lifetime of underwater gel sensors. Because the dynamic bonds that help to self-heal are easily disturbed by water molecules in wet environment, the collaboration of hydrophobic effect and dynamic bonds is considered to be an effective method to achieve underwater self-healability.[56, 59, 61] Fu *et al.* developed an autonomous underwater self-healing hydrogel sensor by introducing the strong dipole–dipole interactions and weak H-bonds (Figure 10c).[59] The hydrophobic effect of dipole-dipole interaction from cyano-groups promote efficient underwater self-heal by removing the water molecules on damaged interface and facilitating the dynamic H-bond rebuilding at the interface. The rapid underwater self-healing capability (98% self-repair efficiency after 1 h of healing) significantly expands their lifetime in unsafe underwater environments. Compared to the underwater self-healing gels based on weak dynamic non-covalent interactions (such as H-bonds, dipole-dipole interaction, electrostatic interaction), the dynamic covalent bonds also endow water-resistant conductive gels with superb underwater self-healing properties, even without the assistance of hydrophobic interaction. For example, utilizing the dynamic reversibility of metal coordination (between the poly(acrylicacid) chain and Al^{3+}) and Schiff base bonds (between chitosan and dialdehyde carboxymethyl cellulose), an underwater self-healing hydrogel sensor was constructed, which reached a 90% self-healing rate in 10 min under water.[63] Besides, boronic ester bonds also show potential in underwater self-healing gels.[73]

In addition to the above properties, the recyclability and 3D printability of underwater sensing gels have also attracted people's attention recently, considering the processing and forming capacity

of gel sensor. The recycling of water-resistant conductive gels is of great significance for protecting environment, saving resources and reprocessing of gel sensors, and the recyclability of gels could be endowed by physical crosslinking. Ethanol is a good solvent that could break the non-covalent physical crosslinking interactions within water-resistant gels. For example, the anti-swelling supramolecular hydrogels based on multiple physical interactions (H-bonds, electrostatic interaction and hydrophobic association) was completely dissolved into a transparent and environmentally friendly adhesive after immersion in anhydrous ethanol for 24 h (Figure 10d).[57] These gel solution dissolved in ethanol can be easily reprocessed to new underwater gel sensor after solvent evaporation, which is beneficial to regeneration of device.[51] As a promising material processing technology, 3D printing allows rapid prototyping of gel sensors with complex and fine structure. One of the methods to realize 3D printing is to endow gels with sol-gel transformation and injectability via physical crosslinking design.[74] Recently, the water-resistant ionogels that are suitable for extrusion-type 3D printing have been developed utilizing their shear-thinning behavior and injectability (Figure 10e).[46-47] However, the research of 3D printability of water-resistant conductive gel has just started, more 3D printing gel materials and design principles need further study.

4. Applications for underwater sensing gels

4.1. Motion perception

Strain sensing mechanism is one of the most widely used sensing mechanisms of conductive gels based sensors. According to the law of resistance, the resistance of conductor depends on its geometric shape, including its length and cross-sectional area. Specially, the resistance of the

conductive gels depends on the geometric deformation (e.g. stretch and compress) under an applied force, and the change in the resistance realizes the strain sensing function of conductive gels. Owing to the strain sensing function and the underwater stability, the water-resistant conductive gels have a broad application prospect in real-time detecting the motion of swimmers and divers as wearable sensors, which are of great significance for visualizing invisible underwater motion.

The movement of the human joint causes the skin to stretch or contract, which drives the geometric deformation of the sensing gel attached on the skin and produces a responsive electrical signal to human motion in real time. As the simplest verification of underwater sensing performance, water-resistant gel sensors are often attached to the knuckle of fingers to monitor their motions in water.[55, 62-63, 66, 72, 75-76] For example, a continuous resistance variation could be detected by underwater gel sensor consisted of carbon nanotubes and double-network hydrogels (CNT@DNHG) when the finger carried out repeated bending and straightening under water (**Figure 11a**).[62] Besides, by fixing theses underwater wearable sensing gels on other parts of human body, various delicate body motions in the whole underwater activity (including swimming and diving) can be clearly recorded and analyzed.[50, 67] Ren *et al.* simulated the detection capacity of water-resistant gel sensor for breaststroke sport with puppet in a water environment (Figure 11b).[67] A full set of basic motions during breaststroke (including gliding, breathing, charging, and kicking), which were simulated by bending the neck, shoulders, elbows, and knees, were clearly detected and easily identified by attaching the hydrogel sensor DN-FT-HCl to the these movable joints. Furthermore, our group monitored the real underwater sport process of volunteer using the full-hydrophobic ionogel sensors, and also obtained a series of real-time and distinguishable detection data, which could even be used to distinguish different swimming strokes of breaststroke and crawl (Figure 11c).[50] The

underwater wearable gel sensors can accurately perceive and recognize the motions of human in water, and the application of motion perception provides valuable reference data for security warning and posture correction of underwater workers.

In addition to the motions of human, the underwater wearable sensing gels also can be used to perceive the motions of other underwater creatures. As a demonstration, a water-resistant gel sensor was applied to successfully capture and distinguish the shark model's various swimming modes, including rest, swimming slowly, fast swimming, leaping out of the water, turning right and turning left, by evaluating the intensity, frequency and duration period of electrical signal (Figure 11d).[50] A similar result was obtained by collecting the output relative resistance variations of MXene/PHEMA hydrogel-based sensor that attached to the left side of the electrical shark model (Figure 11e).[77] Utilizing the application in motion perception, there is also a great potential for underwater wearable sensing gels in studying and tracking the living habits of aquatic organisms.[52]

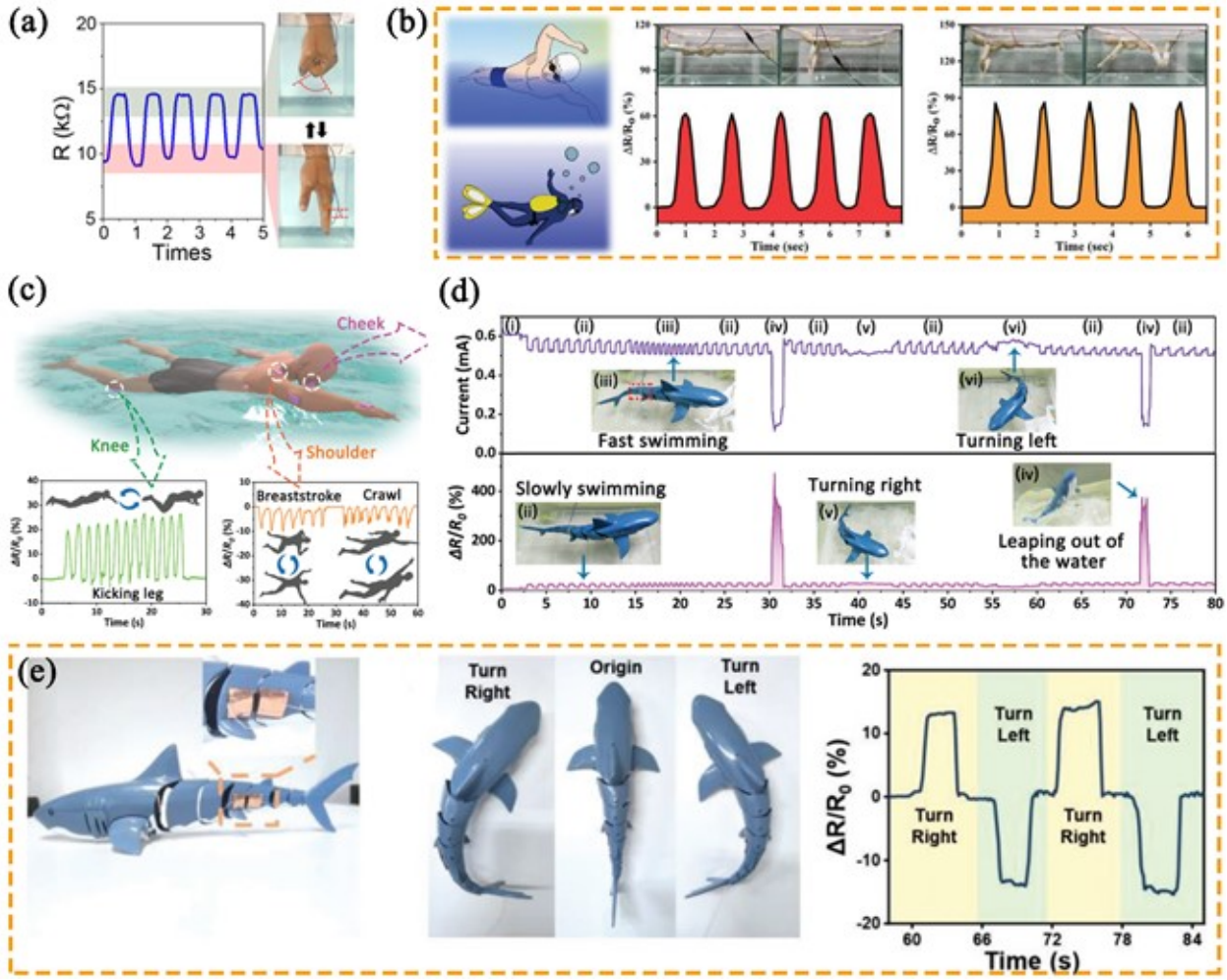

Figure 11. Motion perception. (a) Evolution of resistance of CNT@DNHG for bending/unbending the index finger in water. Reproduced with permission.[62] Copyright 2020 American Chemical Society. (b) Real-time relative resistance changes of DN-FT-HCl hydrogel sensor for underwater human motion detection, including bending elbow and bending knee. Reproduced with permission.[67] Copyright 2021 John Wiley & Sons. (c) Relative resistance variation of the ionogel sensor when monitoring the leg and swimming stroke during swimming by fixing the ionogel sensor on the knee and shoulder. (d) Relative sensing signal of the ionogel sensor monitoring the swimming of an aquatic snake model in the simulated seawater. Reproduced with permission.[50] Copyright 2021 The Royal Society of Chemistry. (e) Relative $\Delta R/R_0$ when the shark model that attached with MXene/PHEMA hydrogel-based sensor moved. Reproduced with permission.[77] Copyright 2022 John Wiley & Sons.

4.2. Health monitoring

With the development of society, there is a booming interest in water-related activities, such as swimming, diving and ocean exploration. However, the special environment of water often accompanied with many hidden dangers, including causing leg cramps, choking on water, and inducing heart disease. As an efficient way of underwater sports management and healthcare, real-time underwater health monitoring is crucial for guaranteeing the safety of swimmers and divers. Due to the good biocompatibility of gels, conductive gel are often used to monitor physiological signals (e.g., pulse signals and bioelectrical signals) of the human body as wearable and biocompatible electrodes. Therefore, the underwater gel sensors with satisfactory underwater stability provide opportunity for the realization of underwater health monitoring in non-invasive mode.

Pulse is an important sign of human health, monitoring the pulse shape features for pulse diagnostic information can understand the health condition of cardiovascular system. Based on strain sensing mechanism, a water-resistant gel based pulse detector was developed for underwater healthcare management, and the pulse frequency and time intervals of volunteer were successfully acquired through this pulse detector (**Figure 12a**).[40] Due to the high sensitivity of gel based pulse detector, the keys to diagnosis the arterial stiffness and vascular aging related healthcare issues, i.e. three distinguishable peaks of percussion wave, tidal wave and diastolic wave, are captured in the pulse signals. In contrast, bioelectrical signal detection is another more commonly used diagnosis method in health assessment and sports management. The bioelectrical signals, including potential changes and electrical currents, generated from muscle movements and nerve activity in living organisms, can be detected by adhering biological electrode on the human epidermal tissue.

Recently, as new high-performance biological electrode, the water-resistant gel sensors have gained attention and progress in the field of underwater electrocardiography (ECG) monitoring, which is relative to electro-cardiac activity and essential to clinic diagnoses.[43, 48-49] For example, utilizing the excellent stability rooted from hydrophobic polymer networks, Wu *et al.* prepared a hydrophobic ionogel as biological electrode, which was attached on the human forearm to detect the ECG signals in an aquatic environment (Figure 12b).[48] Compared to the short service life (less than 10 min) of commercial gel electrode, the hydrophobic ionogel electrode was able to record the stable ECG signals containing distinguishable P wave, QRS complex, and T wave continuously for 30 min under water owing to the strong adhesion ability. The stability of ECG signal during body movement is an important index to evaluate the practicability of biological electrode, especially for underwater application. Attributed to the excellent underwater adhesiveness and compliance with the skin, a stable and high-quality ECG signal without obvious shift of the baseline was captured by underwater gel electrode (butyl acrylate-Acrylic acid- choline acrylate bio ionic liquid-tannic acid gel, which is abbreviated to BACT gel) in continuous bending of wrist (Figure 12c).[60] Electromyography signal (EMG) is a bioelectrical signal associated with muscle contraction, directly reflecting the real-time state of nerves and muscles during body movement. Water-resistant conductive gels show a broad application prospect in the fields of underwater electromyography monitoring, which is of great significance for health and fatigue evaluation of muscle. In addition to be applied for ECG monitoring, the BACT gel electrode also was used to monitor the movements and rehabilitation training of fingers by detecting the EMG signals generated from the contract of wrist flexor muscles (Figure 12d).[60] A high consistency of EMG signal peak and the grip strength could be found in the underwater EMG signals due to the high stability and accuracy of gel electrode.

The excellent performances of water-resistant conductive gel, including underwater sensing, underwater stability, underwater adhesiveness, biocompatibility and softness, enable superior physiological signal monitoring in the underwater environment, providing a feasible path for the health management of underwater activities in real time.

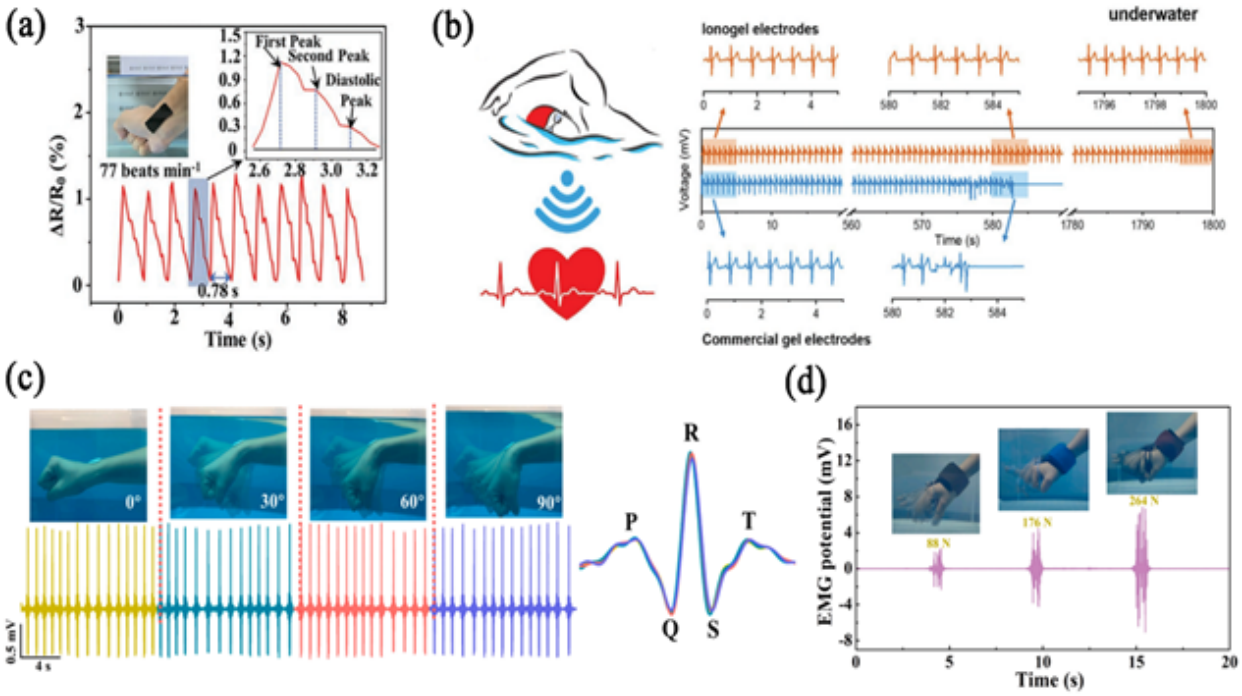

Figure 12. Health monitoring. (a) Pulse signal recorded by SGC based underwater sensors in the underwater environment. Reproduced with permission.[40] Copyright 2022 John Wiley & Sons. (b) Long-term stability of ECG signal detected by commercial gel electrode and ionogel electrode in the aquatic environment. Reproduced with permission.[48] Copyright 2021 John Wiley & Sons. (c, d) ECG signals during the movement of the wrist and EMG signals generated by the different pounds finger trainer recorded by the BACT gel electrode in the underwater environment. Reproduced with permission.[60] Copyright 2022 Elsevier.

4.3. Underwater communications

Diving is one of the most important ways to carry out underwater operation, but it has been plagued by the deficiency in underwater communication materials and technology. Therefore, it is necessary and urgent to develop underwater communication technology in the area of underwater operations, the realization of real-time communication between divers and divers/land personnels will effectively improve the safety of divers and the efficiency of diving operations. The excellent underwater sensing capacity of water-resistant conductive gel provides the basis for divers' communication under water, and some wearable underwater communication devices based on the underwater sensing technology have been developed successfully utilizing water-resistant conductive gels recently. Underwater communication has become an important application of gel based underwater wearable sensing. Depending on the communication mode, there are two types of gel based underwater communication strategies: Morse-code communication and handwriting communication.

Morse code is a time-honored form of digital communication. According to the mechanism of Morse code, the messages consisting of letters and numbers can be represented and transmitted by various sequences of dots and dashes. Inspired by the ability of gel sensor to detect finger motions, the Morse-code communication strategy is developed to transmit messages under water. For example, our group established a underwater communication technology through monitoring finger bending status by hydrophobic ionogel sensor and matching different bending angles (~40 ° and ~70 °) to the ''dots'' and ''dashes'' of Morse code (**Figure 13a**).[50] As a validation, some useful messages for divers, such as "take a 3 min stop" could be sent from underwater by rhythmically and regularly bending finger referring to Morse code. Besides, the Morse-code communication can be performed by matching the electrical signal duration to the two symbols of Morse code. Specifically,

the short period of electrical signal caused by short-time bending finger represents the “dots”, and the long period of electrical signal caused by long-time bending finger represents the “dashes”.[30, 46-48, 59, 61] In this way, the distress signal “SOS” was effectively transmitted in a more easily controlled method (Figure 13b).[47] Furthermore, these raw electrical signals could be translated into visible English letters, and displayed by the screen of the decoder on the ground.[72]

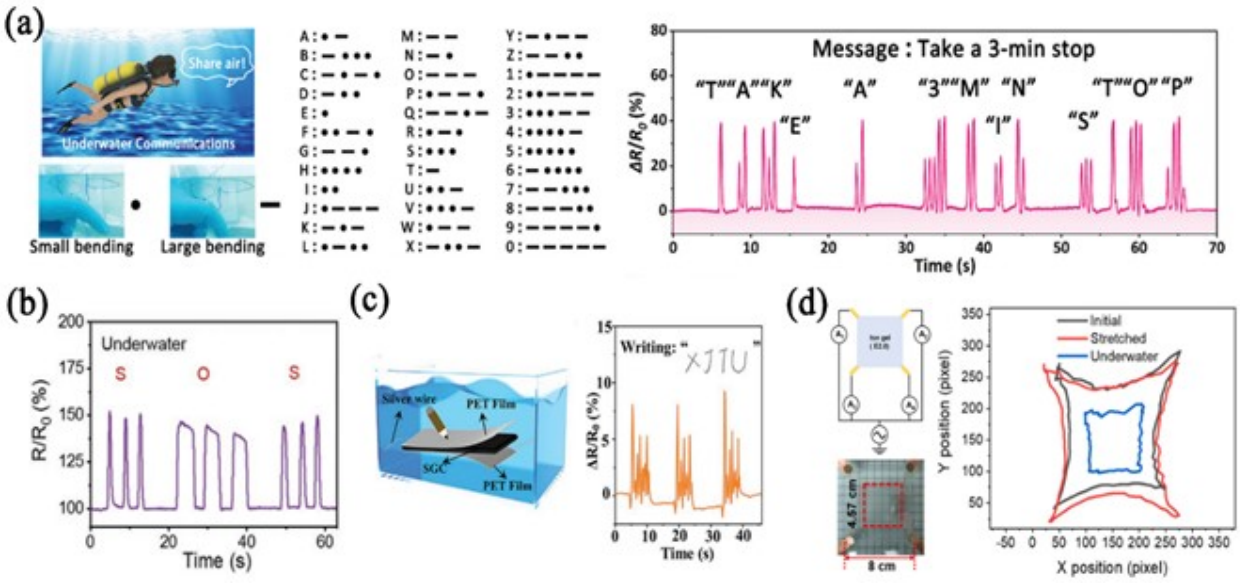

Figure 13. Underwater communications. (a) Underwater communication mechanism based on the Morse code, and sending the message of ‘‘take a 3 min stop’’ by regularly bending the finger attached by an ionogel sensor under water. Reproduced with permission.[50] Copyright 2021 The Royal Society of Chemistry. (b) Ionogel sensor communicates through Morse code under water. Reproduced with permission.[47] Copyright 2021 John Wiley & Sons. (c) Schematic illustration of handwriting board based on the SGC underwater sensors, and the $\Delta R/R_0$ for the letter of “XJTU” by writing on the system. Reproduced with permission.[40] Copyright 2022 John Wiley & Sons. (d) Ionogel touch panel and the drawing results displayed on screen. Reproduced with permission.[79] Copyright 2022 Elsevier.

For handwriting communication, the underwater handwriting board is constructed based on the hydrogel sensor, and the information that needs to communicate can be written directly on the communication board by the sender. During the writing process, each letter or number has its own characteristics, and the underwater gel sensor can detect their unique electrical waveform. Correspondingly, the receiver can deduce the information sent by handwriting based on the detected waveform.[40, 55] Wang *et al.* assembled an underwater handwriting recognition system by sandwiching a conductive gel layer between two PET films, and a dedicated electrical signals of "XJTU" generated by writing on the system was received successfully (Figure 13c).[40] Although handwriting communication is a convenient underwater communication way for the sender, it is difficult for the receiver to recognize the received information quickly and accurately, because the unique signal waveform of each letter is irregular, and even there is individual difference for the same letter written by different writers.[55] Recently, a water-resistive ionogel touch panel that can be used in water was developed by employing four electrodes and function generators. Through monitoring the current change of four electrodes and calculating the relative position, the handwriting path on the ionogel touch panel could be accurately traced and recorded in real time. As a demonstration, the pattern drawn on the ionogel touch panel can be simultaneously displayed on screen under various conditions (initial, stretched, and underwater conditions) (Figure 13d).[79] Obviously, the water-resistant touch panel that can track and reproduce handwriting paths is a promising machine in the field of underwater communication.

Both Morse-code communication and handwriting communication succeed in sending information from underwater, but how to realize the real-time bidirectional communication, especially the

reception and presentation of communication information in the underwater, is still a real and significant challenge in the field of sensing gel based underwater communication.

4.4. Environmental analysis

Perception and analysis of water environment information, such as water temperature, water pressure, salinity, flow rate and so on, is of critical importance for underwater explorative activities and hydrologic monitoring. Besides, the sensing performances of underwater sensor, including sensitivity, signal intensity and stability, are greatly affected by the surrounding water environment, so the measurement of various parameters of water environment will provide basic data for the calibration of the sensing performance, which is of great significance to improve the accuracy of sensor. Thanks to the diverse sensing modes of water-resistant conductive gels, the gel based underwater wearable sensors have shown great potential in the field of water environmental analysis.

Flow state, including velocity and direction, is an important parameter of water environment. Inspired by the flow sensing organ of animals, some ultrasensitive flow sensors were developed by assembling hydrogel and sensing component.[80-83] For example, Moshizi *et al.* prepared a VGNs/PVA hydrogel flow sensor based on PVA hydrogel nanocomposites with a mazelike network of vertically grown graphene nanosheets (VGNs), and the flow sensor was highly sensitive to tiny stimuli underwater, possessing a high sensitivity (5.755 mV (mm s^{-1})$^{-1}$) and extremely low velocity detection (0.022 mm s^{-1}) (**Figure 14a**).[80] In addition, utilizing the ultrahigh strain sensitivity of ionic sensing hydrogel, a hydrogel based vibration sensors that work underwater was designed for detecting the

water wave vibration (Figure 14b).[34] As a result, the tiny fluctuation of water surface induced by dripping of water droplet was detected and recorded clearly by the hydrogel sensors. This vibration sensors based on conductive hydrogel have the potential application in water wave monitoring, which is meaningful for wave warning and the safety of divers and subsea equipment. In addition to the detection of a single water environment parameter, such as the water flow or water wave mentioned above, the simultaneous detection and analysis of multiple water parameters also can be achieved by integrating multiple test units into one gel sensing device. Lately, Cheng *et al.* firstly developed an ionogel based aquatic skin with multi-modality sensing capacities of contact pressure, depth, temperature, and salinity by assembling four iontronic sensing units containing independent interdigitated electrodes in one shared ionically active layer (Figure 14c).[52] Through continuously monitoring the interfacial capacitance from the individual iontronic elements, the multi-modality underwater sensing device attached on the skin of diver as aquatic skin was capable of simultaneously assessing the depth, contact pressure, temperature, and salinity of surrounding water environment altogether when the diver performed underwater suspension and diving activities. This integrated multi-functional environmental sensor will be one of the most promising development directions of underwater wearable gel sensor in the future.

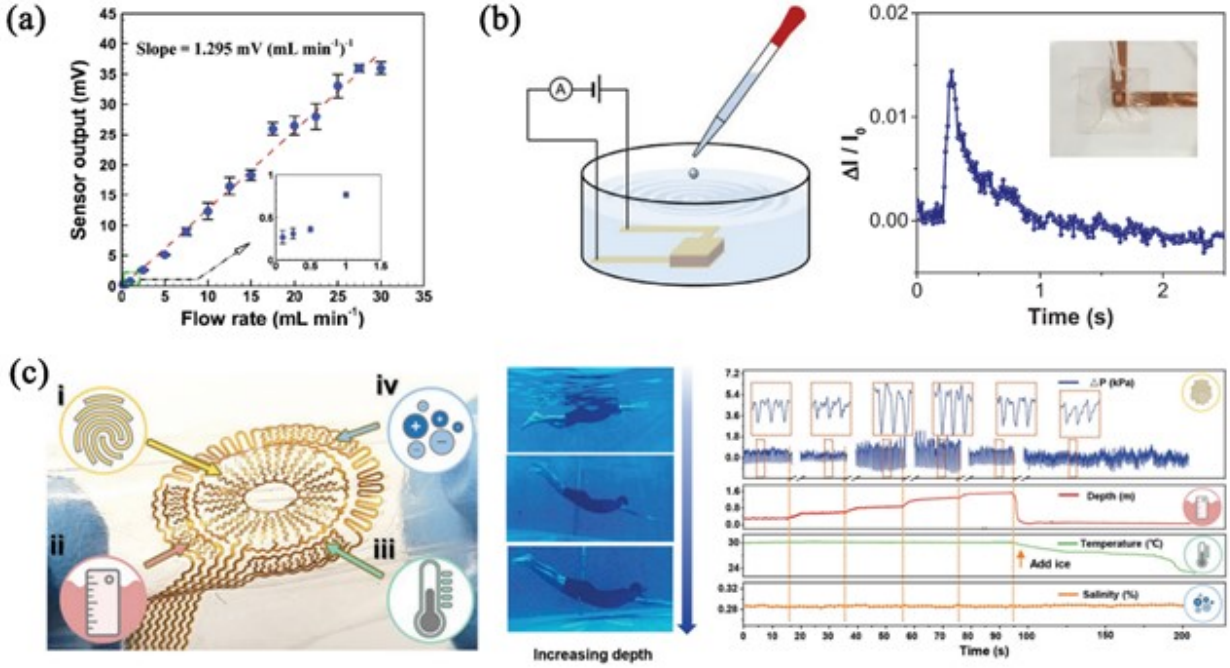

Figure 14. Environmental analysis. (a) Sensing the flow rate by PVA hydrogel based flow sensor. Reproduced with permission.[80] Copyright 2021 John Wiley & Sons. (b) Detection of water wave vibration underneath the water by asymmetric ionic sensing hydrogel. Reproduced with permission.[34] Copyright 2020 John Wiley & Sons. (c) Photographs of aquatic skin with multimodality sensing capacity of contact pressure, depth, temperature, and salinity, and the volunteer performing underwater suspension and diving activities at different depths along with all aquatic skin recordings. Reproduced with permission.[52] Copyright 2022 John Wiley & Sons.

Owing to the stable and diversified underwater sensing ability, excellent mechanical properties in softness and stretchability, the water-resistant conductive gels has a broad application prospect in the field of underwater wearable sensing. In addition to the applications in motion perception, health monitoring, underwater communications and environmental analysis, the underwater gel sensors are also explored and applied in other fields, such as underwater acoustic detection[84-85], underwater optical sensing[37], robotic skin[86] and so on.

5. Summary and Perspectives

Water-resistant conductive gels that maintain structural and functional stability in the aqueous environment hold great promises for underwater wearable sensing. Successful designs for water resistance of conductive gels have been enabled by the rapid advances in materials development and structure innovations. These proposed strategies, including packaging architecture with water-proof materials, designing hydrophobic gel by hydrophobic network, and suppressing swelling by multiple interactions, have been demonstrated to be effective for improving the underwater stability of conductive gels. In addition, the synergetic effects based on hydrophobic interaction and multiple dynamic interactions have been employed to endow conductive gels with underwater adhesiveness and underwater self-healing ability, which contribute to the wearability and reliability of the gel sensor in the aqueous environment. Water-resistant wearable gel sensors that operate robustly in the underwater environment have found extensive applications in many aspects of underwater sensing, including motion perception, health monitoring, underwater communications and environmental analysis and other fields.

Despite the exciting achievements in the area of underwater gel sensors, there are several urgent challenges are yet to be tackled in the future considering they are in the embryonic stage of development. First, the underwater sensing mechanism and model of conductive gels need further study and improvement. Although the water-resistant conductive gels with underwater sensing capacity have been developed successfully, their sensing performance in the underwater environment is generally lower than that on land, especially in the ocean and other practical

scenarios, and the influence mechanism of water environment (e.g. salinity, temperature, water pressure, disturbance of water flow, etc.) on sensing performance is still remaining to be further elucidated, which will provide design guidance for the development of gel sensors with more superior underwater sensing performance. Second, although many reports mention the underwater stability of water-resistant conductive gels in their studies, these evaluation methods are incomplete and unconvincing, focusing more on short-term swelling resistance, while more comprehensive and long-term stability studies are lacking. Therefore, it is necessary to establish normative characterization method and evaluation criteria to study the underwater stability of underwater gel sensors. Third, the design of water-resistant conductive gels with additional functionality to fabricate multifunctional underwater wearable sensors deserves more effort, including the visual perception based on responsive color-changing capacity, the anti-contamination capability based on self-cleaning function, the long operating life based on self-healing ability, the environmental friendliness based on biocompatibility and biodegradability. Fourth, to meet the demands of underwater application in practice, more novel technologies must be developed for water-resistant gel based wearable sensors, such as the use of wireless transmission technology for obtaining signal remotely. The existing wire-connection transmission mode greatly limits the distance that signals can transmit. The progressive wireless transmission technologies combined with mobile terminals could vigorously facilitate their practical usage in underwater condition by real-time data transmission and analysis over long distances. Besides, self-powered technology is also expected to be acquired for weaning off energy dependence. Furthermore, the all-in-one underwater gel sensing system with multiple function units for multi-stimuli perception or/and multi-technology integration is another pending issue. The main limitations for system integration, including eliminating the cross-talks among

different sensing abilities and realizing stable interface connection between the "soft" gel material and the "hard" electronic elements, may be addressed by plane structural engineering, multimodal characterization and advanced material design for soft electronic elements. Challenges and opportunities coexist, the high-performance underwater sensing gels have more potential applications in frontiers, such as the perception system and interactive system of underwater soft robots, early-warning system of sea state. It is well foreseeable that the next-generation underwater wearable sensors based on advanced water-resistant conductive gels will have a profound promoting effect on our underwater activities.

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The authors declare no conflict of interest.

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Underwater wearable sensing is of great significance for improving the safety and efficiency of underwater activities. This review presents the representative design strategies for developing water-resistant conductive gels and their diversified applications in the underwater sensing field as wearable sensors, which provides guidance for promoting the rapid development of gel based underwater wearable sensors.

Keywords: water-resistant, conductive gel, underwater sensing, wearable sensor

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Water-Resistant Conductive Gels toward Underwater Wearable Sensing