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Bionic ordered structured hydrogels: structure types, design strategies, optimization mechanism of mechanical properties and applications

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Natural organisms, such as lobsters, lotus, and humans, exhibit exceptional mechanical properties due to their ordered structures. However, traditional hydrogels have limitations in their mechanical and physical properties due to their disordered molecular structures when compared with natural organisms. Therefore, inspired by nature and the properties of hydrogels similar to those of biological soft tissues, researchers are increasingly focusing on how to investigate bionic ordered structured hydrogels and render them as bioengineering soft materials with unique mechanical properties. In this paper, we systematically introduce the various structure types, design strategies, and optimization mechanisms used to enhance the strength, toughness, and anti-fatigue properties of bionic ordered structured hydrogels in recent years. We further review the potential applications of bionic ordered structured hydrogels in various fields, including sensors, bioremediation materials, actuators, and impact-resistant materials. Finally, we summarize the challenges and future development prospects of bionic ordered structured hydrogels in preparation and applications.

Wider impact

This paper systematically introduces the bionic organisms, structure types, design strategies, mechanical performance optimization mechanisms and wide application prospects in the field of bionic ordered structured hydrogels. At present, most hydrogels face difficulties in their practical applications due to their weak mechanical properties. Bionic ordered structure is a promising new idea to effectively improve the mechanical properties of hydrogels, so it has received extensive attention from researchers. Based on the above discussion, we predict that bionic ordered structured hydrogels will play a key role in advanced fields such as wearable and implantable bioelectronics, tissue engineering, biomedicine, *etc.* This paper summarizes the latest design strategies of specific structures and ordered structures of different bionic organisms, and provides a good reference for the preparation of bionics and advanced engineering materials. Finally, the challenges in manufacturing and future prospects of bionic ordered structured hydrogels and their functions and applications are summarized in order to realize the structural functionalization and functional diversification of hydrogels in the future.

1. Introduction

Hydrogels, with their three-dimensional polymer network structure, have become a critical area of study in various fields, including biomedicine, tissue engineering, and flexible electronic devices. This is due to their excellent biocompatibility, as well as their unique physical and chemical properties and high water content.[1–3] However, the mechanical properties of hydrogels have been found to be inadequate in terms of softness, brittleness, and ability to suffer permanent fracture, thereby hindering the extent to which they can be further designed and applied.[4,5] Consequently, how to improve the mechanical properties of hydrogels has emerged as a critical area of research. Enhancing the mechanical properties of hydrogels has been a focus of researchers in recent years. Several methods have been explored, including introducing energy dissipation mechanisms such as constructing double networks,[6,7] introducing nanocrystals,[8] inducing hydrophobic association,[9] *etc.* Despite their potential, these design strategies have limitations when it comes to improving the mechanical properties of hydrogels.[10,11] Research has shown that these properties are closely linked to the structure of the materials, posing a significant challenge for intrinsic improvements in this area. Nature-inspired research has uncovered that the ordered structures found in the tissues of living organisms are responsible for their exceptional mechanical properties.[12,13] Consequently, designing and producing

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hydrogels with comparable mechanical properties through bionic ordered structures is practical and desirable.

Currently, popular areas of research on bionic ordered structures involve lamellar structures patterned after shells,[14] fasciculate structures mirroring tendons,[10] gradient structures resembling *Mimosa*,[15] array structures similar to biofilms,[16] fiber chain structures that mimic spider silk[17] and so on. Due to their unique structural traits and biomechanical properties, researchers generally employ a variety of constituent materials, construction methods, and structures to prepare bionic ordered structured hydrogels for design purposes. In recent years, researchers have discovered various synthetic methods for constructing ordered structures, including self-assembly,[18] external field control,[19] directional freeze-casting,[10] prestretching,[20] microfluidics,[21,22] 3D printing,[23,24] and electrostatic spinning,[25,26] among others. In addition, scientific researchers have explored the mechanisms by which ordered structures enhance toughness and anti-fatigue properties in hydrogels. Ordered structures increase the cross-link density of the hydrogel network, resulting in synchronized hydrogel force and high mechanical strength,[27,28] which is crucial for preventing mechanical damage during practical use. Typically, stronger materials are more brittle, while weaker materials are more susceptible to deformation.[29] Therefore, effectively combining strength and toughness in hydrogels continues to present a significant challenge. The ordered structure of the hydrogel network enhances external energy dissipation and optimizes the conduction of external forces, leading to a substantial improvement in the hydrogel's toughness.[30,31] A novel approach of constructing ordered structures can significantly enhance the responsiveness and deformation speed of hydrogels for use in practical applications, thereby widening their potential applications in sensors and actuators. Moreover, their superior strength and toughness make hydrogels an advantageous tool in the field of biomedicine.[32–35] Although hydrogels have excellent strength and toughness, they are susceptible to fatigue fractures when subjected to multiple cycles of mechanical loading, making it challenging to maintain their stability and durability as bioremediation materials. Therefore, there is an urgent need to enhance the anti-fatigue properties of hydrogels. To this end, it has been discovered that the ordered and partially crystalline structure within a hydrogel can resist the extension of fatigue cracks more efficiently than amorphous polymer chains, thus improving the anti-fatigue properties of the hydrogel.[36,37] Therefore, the advancement of bionic ordered structures is crucial in enhancing the strength, toughness, and anti-fatigue capabilities of hydrogels.

In this paper, the structure types, design strategies, and optimization mechanisms of the mechanical properties of bionic ordered structured hydrogels are discussed. Subsequently, applications of bionic ordered structured hydrogels are also discussed. In Section 2, five different types of ordered structures are classified according to their structural characteristics and mechanical properties. The typical organisms and their specific structures are also described in detail, in the expectation that they can provide a reference for the preparation of bionic ordered structures. In Section 3 the constituent materials and construction methods required for the common artificial preparation of bionic ordered structured hydrogels are reviewed. In Section 4, we provide a detailed classification and description of the mechanisms for optimizing the strengthening, toughening and anti-fatigue properties of hydrogels using bionic ordered structures. In Section 5, we summarize the applications of bionic ordered structured hydrogels in different scenarios, including sensors, bioremediation materials, actuators and impact resistant materials. Finally, the difficulties and challenges still faced in preparing bionic ordered structured hydrogels are presented, and an outlook on future research on bionic ordered structures is given. It is sincerely hoped that our work will provide a valuable reference for the preparation of bionic ordered structures and the study of the mechanical properties of hydrogels.

2. Types of bionic ordered structures

Nature provides an intriguing source of inspiration for improving the mechanical properties of hydrogels, as organisms in nature often display superior mechanical performance due to their ordered structures. In this section, we introduce three main types of ordered structures in biological soft tissues: lamellar, fasciculate and gradient (Fig. 1), and two other novel types of structures: array structure and fiber chain structure. And the bionic organisms and their characteristics of different ordered structured hydrogels are described in detail.

2.1. Lamellar structures

Lamellar structures are multilayered phases formed by stacks of soft materials.[41,42] This lamellar microstructure is a common feature found in many living organisms and is often associated with excellent mechanical properties.[14,20] As a result, there has been growing interest in studying the lamellar structures present in biological tissues and applying them to hydrogels to enhance their mechanical properties.

The unique biological tissue structures of wood, lobster, and human bones have received significant attention from researchers exploring bionic structures.[30,43–46] Wood, in particular, is a classic example of an ordered lamellar structure found in plants, which is created by the highly ordered arrangement of ultra-fine filaments. These dense microfibers not only bind to the lignin matrix but also guide cell growth and display a deposition phenomenon, resulting in wood's high tensile resistance.[36,47,48] The arrangement of microfibers in different types of wood can vary significantly, affecting cell growth and distribution within trees, subsequently influencing the mechanical properties of wood.[49–51] Besides plants, animals also have ordered lamellar structures in their biological tissues. For instance, the soft membrane tissue of lobster exhibits great toughness and damage resistance due to the chitin fibers' orderly arrangement, forming a multi-level ordered structure. In each layer, the chitin fibers are highly oriented and the rotation angle between each neighboring planes is almost the same, so that the soft membrane has a certain tensile resistance.[36,46,52] The ordered lamellar structure present in bone tissue has also attracted the attention of

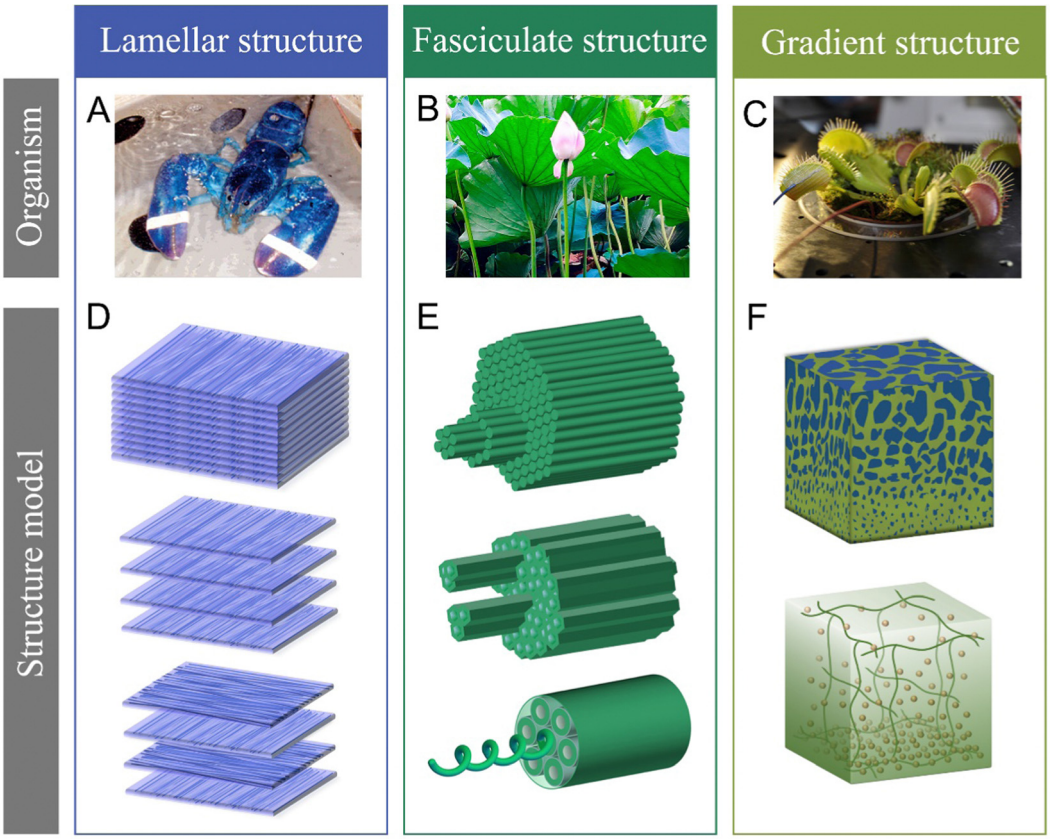

Fig. 1 By imitating three organisms (A) lobster (figure reproduced with permission from American Chemical Society),[38] (B) lotus flower (figure reproduced with permission from American Chemical Society),[39] and (C) *Dionaea muscipula* (figure reproduced with permission from Elsevier),[40] respectively, the researchers have prepared bionic (D) homogeneous and heterogeneous lamellar structures, (E) long strips and honeycomb and spiral fasciculate structures, and (F) structural and compositional gradient structures.

researchers exploring bionic structures in the human body. The compact bone, which is responsible for providing strength and support to long bones, is hierarchically organized across a range of length scales from the microscopic molecular level to the macroscopic level. This organization is characterized by bone blocks containing layers of periodic collagen fibers, which give rise to the distinct and ordered lamellar structure. This specific structure results in remarkable compression and bending resistance, greatly enhancing the bone's overall mechanical properties.[20,53–55]

The prevalence of ordered lamellar structures in organisms provides researchers with opportunities to enhance the mechanical properties of hydrogels by imitating such structures. Bionic lamellar structure hydrogels are generally fabricated by stacking nanosheets to form a lamellar structure. In addition, due to the different internal orientation of the lamellar structure, we classify bionic lamellar structure hydrogels into two types, namely homogeneous lamellar hydrogels and heterogeneous lamellar hydrogels. Homogeneous lamellar hydrogels refer to bionic hydrogels composed of two-dimensional planes featuring the same orientation (Fig. 2A).[47] These hydrogels are typically prepared from highly ordered nanofibers. The fibers inside the hydrogels are arranged in the same direction and the fibers are closely bonded, which enhances the binding ability between hydrogel molecules, so they show high anti-fatigue properties.[47,56,57] Homogeneous lamellar hydrogels consist of two-dimensional planes with consistent orientations, making them prone to deformation or tearing when subjected to forces that do not align with the structural orientation, resulting in weak tearing resistance.[58] To address this concern, researchers have developed heterogeneous lamellar hydrogels with specific orientations between composite layers (Fig. 2B).[46] Examples include a cross lamellar structure, formed by two-dimensional planes perpendicular to each other and an angle lamellar structure formed by two-dimensional planes with varied orientations.[59] Hydrogels with an orthogonal lamellar structure exhibit high tear resistance due to the angle formed between the layers that hold the hydrogel together and effectively disperse forces, preventing crack growth.[46,59,60] For instance, the human cornea withstands intraocular pressure owing to its orthogonal lamellar structure. Inspired by this, researchers have constructed orthogonal lamellar hydrogels comprised of multilayer two-dimensional planes arranged perpendicular to each other, resulting in a highly ordered and aligned structure.[59,61]

To sum up, bionic lamellar structures hold great potential for enhancing the mechanical properties of hydrogels. This is because the structure's differences in two dimensions facilitate the hydrogel's ability to deflect the directional expansion of

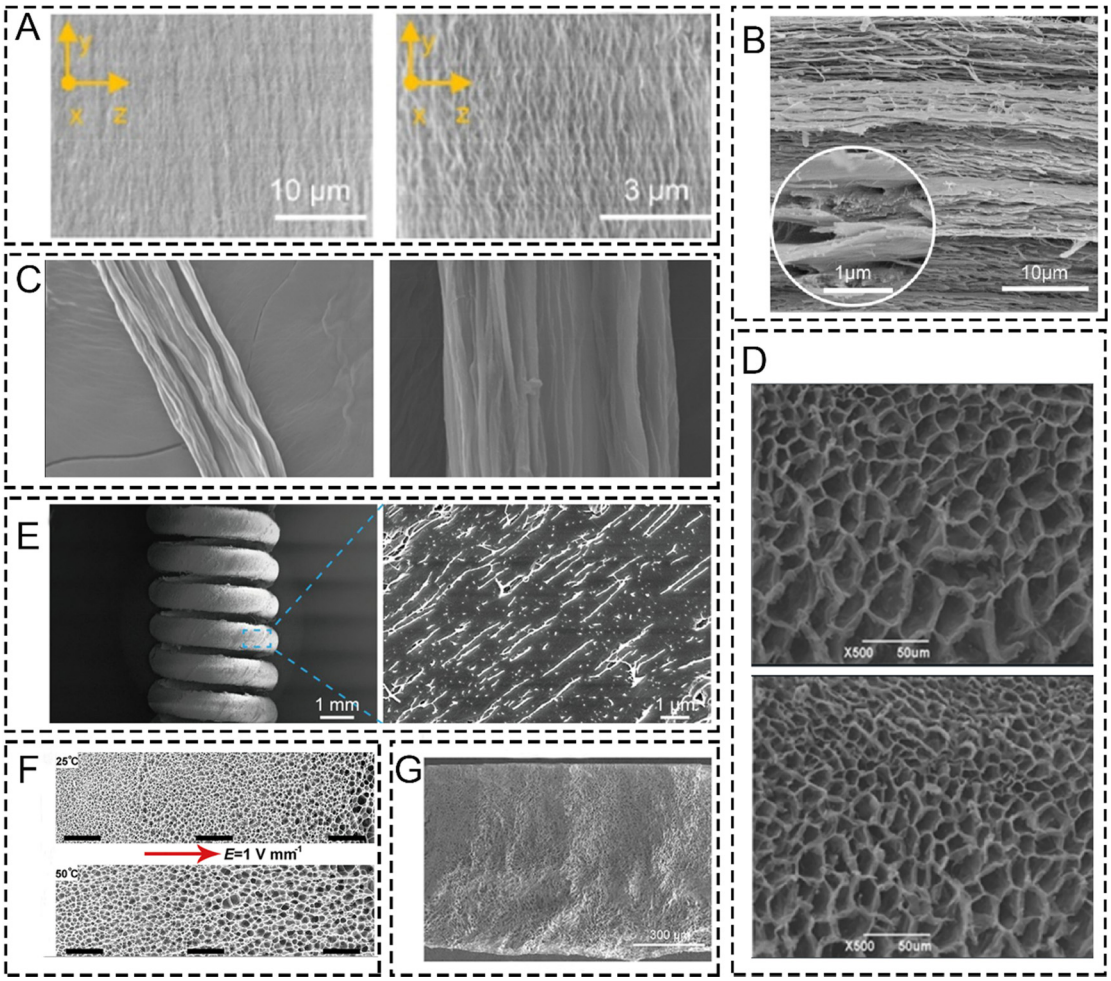

Fig. 2 Bionic ordered structured hydrogels exhibit various types of ordered structures under a scanning electron microscope. These include the lamellar structure, which consists of (A) homogeneous lamellar structures of the same orientation (figure reproduced with permission from American Chemical Society),[47] as well as (B) heterogeneous lamellar structures of hydrogels showing different orientations (figure reproduced with permission from Elsevier).[46] In addition, there are (C) long strips consisting of fiber bundles showing average diameter (figure reproduced with permission from American Chemical Society),[76] (D) honeycombs made up of a mixture of various substances (figure reproduced with permission from Elsevier)[80] and (E) spiral structures produced by the continuous stretching, twisting and coiling process of hydrogels (figure reproduced with permission from American Chemical Society).[69] And there are also (F) pore size gradients (figure reproduced with permission from American Chemical Society)[87] and (G) cross-sectional image of the compositional structure (figure reproduced with permission from Elsevier).[94]

cracks during the fracture process, thus leading to increased strength, toughness, and anti-fatigue properties.

2.2. Fasciculate structures

Fasciculate structures are geometric structures formed by uniform mass monomers that attract or interact with each other such as long strip structures, honeycomb structures and spiral structures.[62–64] Such structures are commonly found in biological tissues and studies have shown that both the fasciculate and lamellar structures contribute to improved tensile strength and elasticity in biological tissues.[65–67] Hence, bionic ordered fasciculate structure hydrogels could be developed, given the comparable properties of hydrogels and biological tissues, to improve their mechanical properties.

The fasciculate structure is present in humans and some plants.[62,67] The ordered fasciculate structures that exist in the human body are muscles and tendons.[66,68] Specifically, the ordered fasciculate structures consist of a large number of fibers arranged unidirectionally.[65] Human muscle fibers are longitudinally arranged and can align in a 3D fashion to form fiber bundles. Furthermore, these structures are wrapped by connective tissues. The fasciculate structures enhance muscle toughness, enabling it to handle higher stresses.[66,69,70] Tendons, on the other hand, consist primarily of parallel collagen fiber bundles that form their fasciculate structure. Intertwining of each collagen fiber bundle occurs, facilitating transmission of tension throughout the tendon and imparting significant energy dissipation capabilities.[68,71] Besides the human body, small fasciculate structures are also present in plant tissues.[72,73] Lotus is a prime example of plants that possess such biomimetically inspired structures. Lotus fibers exhibit a spiral arrangement of fiber bundles formed by joining several monofilaments. On the surface of the fasciculate structure formed by these monofilament unions, there is a

considerable number of slit holes and unevenness, leading to high tensile resistance and energy dissipation capabilities.[39]

Hydrogels with disordered fasciculate structures often do not possess the mechanical properties necessary to meet the requirements of their applications. Consequently, researchers have employed a bionic approach inspired by natural organisms to create various ordered fasciculate structure hydrogels. These include long strip, honeycomb, and spiral ordered structured hydrogels. Long strip ordered hydrogels display a filamentous or long striped appearance (Fig. 2C).[74–76] When long strips of nanoscale hydrogels are arranged in parallel by several monomers and packed into a bundle, they can be observed to exhibit a circular morphology in cross section.[50,74,77,78] The excellent mechanical properties of the monomers themselves lead to high tensile strength and modulus of elasticity observed in this structure. Moreover, each monomer disperses stress when aggregated into bundles.[77] For instance, researchers developed long strip ordered structured hydrogels, whose high tensile capacity was attributed to the dispersion of stress and transfer to each fiber.[74] The microstructure of the honeycomb ordered hydrogel exhibits a closely packed polygonal pore-like structure (Fig. 2D).[62,79,80] Researchers discovered that the honeycomb ordered structure provides additional space within the hydrogel. When this honeycomb ordered structure is exposed to mechanical stress, the thin walls of the honeycomb bear most of the load, while the matrix facilitates stress transfer.[81] Consequently, the honeycomb ordered hydrogel exhibits improved toughness and deformation resistance.[10,81,82] For example, a continuous network of nanofibers was used to construct a bionic honeycomb ordered hydrogel, taking inspiration from the microstructure of tendons. When subjected to external force, the stress was transferred between individual proto-fibers. This effectively transmitted the stress throughout the entire network and prevented slippage between fibers, leading to higher strength.[10] Spiral ordered hydrogels have a distinctive curled appearance compared to the previously mentioned bionic ordered fasciculate structure hydrogels (Fig. 2E). These hydrogels are comprised of interconnected nanoscale monomers with a lengthy linear mechanical region.[69] When placed under a tensile force, their spiral ordered structure undergoes a specific deformation that increases ductility and improves energy dissipation capacity.[39,83] An example of such a hydrogel was the spiral ordered structure inspired by lotus fibers, which was formed under the influence of external forces. Its internal fibers were ordered and twisted to form a spring-like coiled structure.[69] The close proximity of adjacent spiral loops contributes to the hydrogel's superior tensile properties.[39,84]

In summary, hydrogels that feature bionic ordered fasciculate structures display superior mechanical properties compared to disordered structured hydrogels. This is attributed to their tightly connected forms, which are predominantly aligned in a single direction and exhibit clear directionality.

2.3. Gradient structure

A gradient structure is one in which the structure or the composition exhibits a gradient of change, which can be made either as steps or non-abrupt.[85,86] The gradient variation in both the structure and composition of a gradient structure allows for a regular gradient variation in its mechanical properties. This regular gradient variation facilitates the effective distribution and matching of local mechanical properties in the constituent. The gradient structure found in many organisms in nature effectively enhances their mechanical properties to improve their adaptation to environmental changes. Thus, the researchers prepared two different bionic gradient structured hydrogels according to their gradient variations, namely structural gradient hydrogels (Fig. 2F)[87–90] and compositional gradient hydrogels (Fig. 2G).[91–94] The bionic gradient structure of the hydrogel enhances not only its mechanical properties, but also gives rise to mechanical gradients that increase its anisotropy due to the variation in structure and composition.

The gradient structures found in nature, such as those in flycatchers, bamboo, and cartilage, provide exceptional strength and toughness. For instance, flycatchers exhibit remarkable agility in capturing insects within seconds. This rapid motion is thought to be related to the accumulation and rapid release of energy brought about by its gradient structure.[95] Furthermore, bamboo fibers possess a radial gradient structure that increases from the bamboo's inner surface to its outer surface. By optimizing its radial gradient, bamboo exhibits excellent toughness and thus maximizes its bending stiffness, resulting in the ability to bend without breaking.[92,96] In addition to bionic plants, the human body contains cartilage tissue with a layer-specific gradient structure. The structural cartilage tissue functions as a load-bearing, cushioning, and lubricating agent to protect the cartilage from friction.[97] The gradient structure of organisms enhances not only their mechanical properties but also gives some organisms good driving behaviors, such as the movement of octopus tentacles, the closing of *Mimosa* leaves, the insect-catching behavior of flycatchers *etc.* For example, when *Mimosa pudica* leaflets were touched they immediately close. This is due to the uneven distribution of water caused by the gradient changes in their internal structure, resulting in swelling of the upper part, bending of the lower part, downward movement of the petiole and closing of the leaves.[15,98]

Bionic gradient structures inspired by the above-mentioned organisms were prepared to give the hydrogels a gradient modulus that allows them to produce a greater amount of deformation when subjected to pressure. This enables the hydrogel to withstand high compressive strengths and to have better mechanical properties. In bionic structural gradient hydrogels, the gradient change pertains to a spatially distributed microstructure with a gradient-like distribution.[86–88] One of the most representatives of these is the pore size gradient hydrogel, in which pore sizes change along a gradient pattern from large to small or small to large. The formation of this pore size variation can be achieved in two ways. One is achieved by controlling the distribution of the internal components through external conditions and thus directly preparing an inhomogeneous network.[95] The other is a homogeneous network, which is then subjected to an inhomogeneous external treatment to break up the internal cross-linked structure to form an inhomogeneous network.[99] After research, it was found

that both methods have their advantages. While the former is relatively easy to implement, the post-processing method is more adaptable and flexible. All techniques can be employed to modulate the hydrogel's network structure and mechanical properties locally by regulating its pore size configuration.[86] It is therefore possible to generate different stiffnesses and yield stresses in different areas of the hydrogel, resulting in better tensile and toughness resistance.[88,89,97] Bionic pore size gradient hydrogels offer enhanced mechanical properties, while also having anisotropy.[15,87,90,95] This is due to the variation in pore sizes within the hydrogel, which allows it to be unevenly stressed when subjected to external stimuli and is capable of producing different deformations in different areas. As an illustration, gradient structure hydrogels inspired by *Mimosa pudica* leaflets could respond to temperature changes due to a gradient distribution in their centers that induced asymmetric contraction.[15] In addition to this, hybrid gradient hydrogels are produced by copolymerising two or more monomers in different proportions to produce a gradient. During homogeneous transition of its hybrid structure, a modification in performance can be achieved.[86] Consequently, the hybrid structured gradient hydrogel can meet the demand for additional properties and significantly enhance the hydrogel's mechanical properties and stability. For example, Jin *et al.* prepared a hybrid structured gradient hydrogel by copolymerizing a mixture of two monomers, protocatechuic acid (PCA) and calcium alginate (CaAlg). The content of PCA gradually decreased from the inside to the outside and the content of CaAlg gradually increased from the inside to the outside, thus achieving the effect that the inner layer adhered, while the outer layer was not contaminated by oil, and this gradient inhomogeneous hydrogel had greater mechanical stability than homogeneous hydrogels.[86]

The gradient variation of a bionic composition gradient hydrogel refers to the process by which the arrangement of certain constituents within the hydrogel exhibits a density gradient;[92] these include ions, particles *etc.* Within bionic composition gradient hydrogels, the internal particles exhibit greater flexibility compared to other macromolecular substances. This quality facilitates energy dissipation by enabling faster moving deformations, thereby significantly enhancing the hydrogel's mechanical strength.[91,93,94] The most common bionic composition gradient hydrogels are the ionic gradient hydrogels, which exhibit outstanding properties such as antibacterial actions, electrical conductivity, *etc.*[91,94] Thus it greatly expanded the applications of hydrogels. However, the contribution of ions to the mechanical properties of hydrogels is not very significant. In contrast to ions, some particles can also act as cross-linking agents to form a more stable structure through cross-linking, thus better enhancing the mechanical properties of the hydrogel.[92] For example, a bamboo-inspired bionic particle density gradient hydrogel was prepared through the distribution of polyacrylamide and silica particles in a gradient structure within the hydrogel. The incorporated silica particles acted as a physical cross-linking agent, effectively dissipating the mechanical energy of external loads and exhibiting exceptional mechanical strength and bending capacity.[92]

In summary, the bionic gradient hydrogel can improve its mechanical strength effectively through its unique internal structure. Unlike lamellar and fasciculate structures, the gradient structure provides better anisotropy to the hydrogel, enabling it to bend or deform rapidly in response to external stimuli.

2.4. Other structure types

The three common structures that exist in living organisms are the lamellar, fasciculate, and gradient structures. Researchers widely use lamellar structures in preparing bionic ordered structured hydrogels. This is because of lamellar structures' high compressive strength, shear strength, and mechanical stability. However, the lamellar structure has limitations such as significant disparities in mechanical properties along different directions, interlayer delamination, and complexity in preparation methods.[100] Therefore, researchers have explored additional bionic ordered structure types, such as array structure and fiber chain structure. In contrast to the aforementioned common structures, these newer types offer greater malleability, more detailed classification, and specialized applications.[17,101–103]

The array structure is commonly observed on natural biofilm surfaces, including the phospholipid bilayer array and epithelial cell array created by phospholipids found on cell membranes. It refers to the structured array formed by hydrogel monomers or polymer units in a specific sequence, spacing and direction on the surface or inside of the hydrogel.[17,101,104] Researchers have achieved bionic ordered array structure hydrogels with exceptional water permeability, mechanical properties, and programmable responsiveness by applying this natural structure through photolithography, ultraviolet masks, and other techniques.[17,105] The mechanical property enhancement principle of an array-structured hydrogel involves the uneven transmission of mechanical stress.[17] As it differs slightly from other ordered hydrogel structures, this mechanism inhibits the hydrogel from achieving significant mechanical strength.[106] However, the unique surface layer order in array hydrogels makes them valuable in various fields, including tissue engineering scaffolds, drug delivery systems, sensors, and actuators.[16,17,101,102,104,105]

The fiber chain structure is prevalent in several naturally existing flexible filamentous structures, including spider silk's protein distribution and the cytoskeletal protein fibers in cells.[103] The fibrous chain structure comprises van der Waals forces or hydrogen bonds between molecular chains, without any robust chemical cross-linking, except for some protein fibers.[103] Unlike the uniform transmission of force to increase strength in a fiber bundle structure, the principle of enhancing hydrogels with a fiber chain structure is based on the intermolecular interactions between molecular chains. The degree of order is relatively low compared to that of a fasciculate structure, which provides excellent toughness to the fiber chain structure hydrogel.[103] The transformation of crystalline and amorphous domains in the microstructure promotes the dissipation of force. This is because amorphous domains may be forced to form an ordered arrangement during stretching providing high stretchability and strength. When the stretched fibers are released, the temporary ordered molecular chains

will relax yet swiftly restore their initial orientation with the aid of water present in the fibers. However, the crystal domain acts as a physical crosslinking point, thereby enhancing the mechanical strength of the hydrogel.[107] The fiber chain structure's high stretchability and easy recovery characteristics make it a commonly used material in highly elastic fields, such as cushions and arresting cables. Moreover, when fiber chains are stretched, the increased molecular orientation enhances conductivity in specific materials, making them ideal for high-precision sensors, flexible electronic devices, and related applications.[103]

3. Design strategies of bionic ordered structured hydrogels

Recently, scientists have become more interested in the development of bionic ordered structured hydrogels, which draw inspiration from the ordered structures found in organisms. This section will provide a brief overview of the composition materials and construction methods of bionic ordered structured hydrogels. The bionic ordered structure is created by using a composition material-assisted construction method, which effectively fixes the ordered structure and leads to the hydrogel's exceptional mechanical properties.[10,36,56,65] To classify the composition materials used in the construction of bionic ordered structured hydrogels, we categorize them into nanomaterials (0D, 1D, and 2D) and other materials, such as polysaccharides, monomeric molecules, and synthetic polymers. This paper outlines four primary methods for constructing bionic ordered structured hydrogels: self-assembly, external field control (such as electric and magnetic fields), directional freeze-casting, and prestretching. Additionally, we introduce five novel construction methods, including microfluidics, 3D printing, electrostatic spinning, welding, and phase separation. Table 1 provides an overview of various bionic organisms, the types of bionic structures they produce, and the composition materials and construction methods used to create bionic ordered structured hydrogels as reported in the literature. Given the wealth of information provided in Table 1, it is evident that there are significant opportunities for designing and producing highly ordered structured hydrogels inspired by bionic organisms.

3.1. Constituent materials with bionic ordered structured hydrogels

Materials used in the construction of bionic ordered structured hydrogels can be classified into two categories: nanomaterials and other materials. Within the category of nanomaterials, there are three subcategories: 0D materials (such as nanoparticles), 1D nanomaterials (including nanowires, nanotubes, and nanofibers), and 2D nanomaterials (such as nanosheets). Other commonly used materials include polysaccharides, monomer molecules, and synthetic polymers. These materials are used either as the foundation for the construction of bionic ordered structured hydrogels or to reinforce the ordered structure.

0D nanomaterials. Bionic ordered structured hydrogels are often constructed using 0D nanomaterials such as SiO_2 nanoparticles,[18,115,116] magnetic nanoparticles,[19] and lithium saponite nanoclay particles.[87] For example, SiO_2 nanoparticles have been arranged into densely packed hexagonal structures through non-covalent interactions, such as hydrogen bonding and hydrophobic interactions and have served as the foundation for the construction of bionic ordered structured hydrogels.[115]

1D nanomaterials. Nanowires (hydroxyapatite (HAP) nanowires),[36] nanotubes (carbon nanotubes (CNTs)),[117] and nanofibers (cellulose nanocrystals (CNCs),[118] cellulose nanoprimary fibers (CNFs),[119] and bacterial cellulose (BNC)[39,120]) are common 1D nanomaterials used in constructing bionic ordered structured hydrogels. Nanowires such as HAP nanowires are highly biocompatible and can be assembled into hierarchical ordered structures, making them popular for constructing highly ordered nanostructures.[36] Nanocellulose, a natural, abundant macromolecule, has gained attention due to its eco-friendliness and versatility. Adjacent nanofibers have the ability to form hydrogen bonds, which can support the ordered structure.[119]

2D nanomaterials. Nanosheets, such as MXene nanosheets,[57,81,121] graphene oxide (GO) nanosheets,[113,122–124] and titanium dioxide nanosheets (TiNS)[110,125] are commonly used in constructing ordered structures. For example, GO is a nanofiller that can enhance and stabilize the ordered hierarchy of hydrogel networks due to its extensive surface area and polarity functions.[113,122,123]

Other materials. For example, polysaccharide materials such as alginate,[20,126] chitosan,[65,111] have many hydrogen bonding sites that drive fiber formation and are crucial to the development and function of ordered composites.[65,126] Synthetic polymers, meanwhile, utilize internal hydroxyl groups and hydrophilic substances to create physical and chemical cross-linked network structures. Due to their hydrophilic nature, these materials can be used to design ordered crystalline structures that enhance the strength, toughness, and anti-fatigue properties of bionic ordered structured hydrogels.[10,62]

3.2. Construction methods of bionic ordered structured hydrogels

Based on the unique structures found in natural tissues, constructing bionic ordered structures through artificial synthesis is an effective approach for enhancing the mechanical strength, toughness and anti-fatigue properties of hydrogels. Over the past few years, researchers have developed various structural engineering methods to construct bionic ordered structured hydrogels. These methods include self-assembly, external field control, directional freeze-casting, mechanical prestretching, and other novel techniques. These approaches offer a wide range of options for the development of bionic ordered structured hydrogels.

3.2.1. Self-assembly. Self-assembly is a popular approach for preparing bionic ordered structured hydrogels. This method is gaining increased attention from scientists as it does not rely on external forces for implementation.[58,127–129] Self-assembly typically follows a bottom-up process in nature, where simple

Table 1 Bionic organisms, bionic structure types, constituent materials and construction methods of different bionic ordered structured hydrogels

Biological classification	Bionic organism	Bionic structure type	Material category	Constituent material	Construction method	Ref.
Animal	Lobster belly	Lamellar structure	2D nanomaterials	GO	Directional freeze-casting-assisted salting out	108
	Mussels	Lamellar structure	1D nanomaterials	nHA	—	109
	Mussels	Lamellar structure	1D nanomaterials	PFeCNT	Magnetic field control	14
	Sea jellies, seastars, sea anemones, and coral	Gradient structure	0D nanomaterials, polysaccharides	LAPONITE®, Alg	3D printing	93
	Octopus-tentacles	Gradient structure	2D nanomaterials	Nanosilver flakes	Wettability	90
Plant	*Dionaea muscipula*	Gradient structure	2D nanomaterials	GO	UV-induced	95
	Mimosa leaves	Gradient structure	1D nanomaterials	TCNCs	Electric field control	98
	Mimosa leaves, pine cone	Gradient structure	0D nanomaterials	Lithium saponite	Electric field control	87
	Bamboo	Gradient structure	0D nanomaterials	Silica particles	Self-heating	92
	Wood	Lamellar structure	Synthetic polymers	PVA	Directional freeze-casting	51
	Lotus	Fasciculate structure	1D nanomaterials	BC	—	39
Human body	Articular cartilage	Lamellar structure	2D nanomaterials	TiNS	Magnetic field control	110
	Articular cartilage	Lamellar structure	Polysaccharides	Chitosan	Electric field control	111
	Tendon	Lamellar structure	Polysaccharides	Alginate	Prestretching	112
	Tendon, ligaments	Lamellar structure	Polysaccharides	Alginate	Prestretching	44
	Muscles	Lamellar structure	Synthetic polymers	PVA	Prestretching	56
	Muscles	Lamellar structure	2D nanomaterials, synthetic polymers	PVA, MXene	Directional freeze-casting	57
	Muscles	Lamellar structure	2D nanomaterials, synthetic polymers	PVA, MXene	Freeze–thaw	50
	Biological tissue	Lamellar structure	Monomer molecules	DGI	Self-assembly	58
	Skeletal muscle, tendon, and cartilage	Lamellar structure	Synthetic polymers	PVA	Directional freeze-casting-assisted annealing	62
	Tendon, cartilage	Lamellar structure	1D nanomaterials	Cellulose nanofiber	Prestretching, welding	59
	Natural bone	Lamellar structure	1D nanomaterials, polysaccharides	HAp, SA	*In situ* mineralization	43
	Cartilage	Lamellar structure	1D nanomaterials	HAp	Self-assembly	36
	Tendon, ligaments	Lamellar structure	Polysaccharides	Alginate	Prestretching	20
	Cartilage, tendon, ligaments	Lamellar structure	Polysaccharides	Chitosan	Prestretching	65
	Heart valves	Lamellar structure	2D nanomaterials, synthetic polymers	PVA, GO	Directional freeze-casting-assisted annealing	113
	Tendon	Fasciculate structure	Synthetic polymers	PVA	Directional freeze-casting-assisted salting out	10
	Muscles	Fasciculate structure	1D nanomaterials	TCNCs	Consecutive stretching, twisting, and coiling	69
	Muscles, ligaments, nerves	Fasciculate structure	1D nanomaterials	CFs	*In situ* free radical polymerization	114
	Skeleton, skin	Fasciculate structure	Polysaccharides	Chitosan, gellan gum	Self-assembly	77
	Heart, brain, spinal cord	Fasciculate structure	Monomer molecules	Peptide micromolecule	Self-assembly	74
	Osteochondral	Gradient structure	1D nanomaterials, polysaccharides	nHA, chitosan	Iterative overlaying, freeze-drying	89
	Articular cartilage	Gradient structure	0D nanomaterials, synthetic polymers	HA, PVA	Freeze–thaw, annealing	97
	Articular cartilage	Gradient structure	0D nanomaterials, synthetic polymers	PVA, Fe_3O_4	Magnetic field control, freeze–thaw, and annealing	30
	Human receptors	Gradient structure	Polysaccharides	Chitosan	Electric field-assisted free radical polymerization	94

GO: graphene oxide; nHA: nanohydroxyapatite; PFeCNT: CNT-Fe_3O_4 nanohybrids; Alg: algae-derived alginate; Lap: smectite silicate nanodisk clay; TCNCs: tunicate cellulose nanocrystals; PVA: polyvinyl alcohol; BC: bacterial cellulose; TiNS: titanate nanosheet; DGI: dodecylglyceryl itaconate; SA: sodium alginate; and CFs: carbon fibers.

components, such as molecules, nanomaterials, micron or larger-scale substances are spontaneously formed hydrogels with stable and ordered structures through non-covalent interactions or other external forces.[58,130–133] Self-assembly technology commonly utilizes shear-induced self-assembly[36,74] and a self-assembly template[18,115,116,134] to construct bionic ordered structures. Shear-induced self-assembly involves inducing the spontaneous formation of highly ordered continuous nanofiber structures along the injection direction through the shearing force of the syringe, providing a foundation for constructing bionic ordered structured hydrogels.[36,74] Self-assembly templates, in contrast to shear-induced self-assembly that requires a high injection direction, are a more convenient and faster method.[18,58,74] Self-assembled templates utilize nanoparticles to form ordered arrangements of structures through non-covalent interactions (hydrogen bonds, hydrophobic interactions, van der Waals forces, *etc.*). This ordered arrangement of nanoparticles can serve as a removable template for the creation of a hydrogel with a bionic ordered porous structure (Fig. 3A).[18,116]

3.2.2. External field control. External field control means that under the action of an applied electric or magnetic field, 0D nanoparticles (magnetic nanoparticles, nanoclay particles,

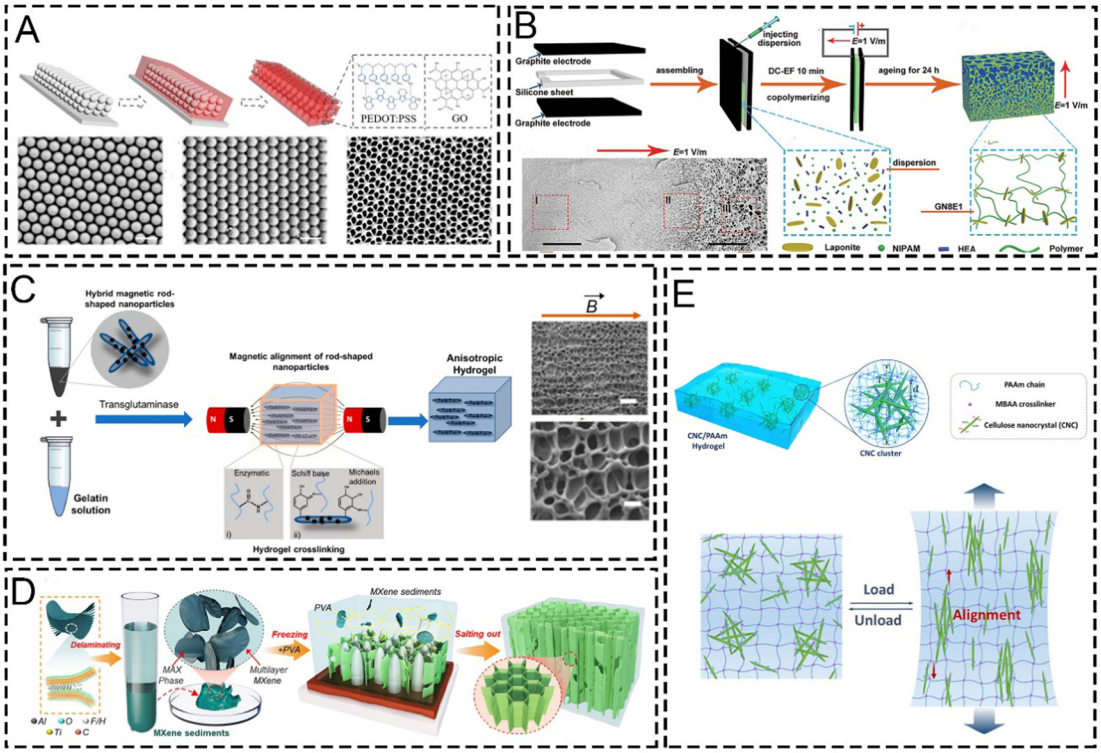

Fig. 3 The method of constructing bionic ordered structured hydrogels through (A) a self-assembly template (figure reproduced with permission from Wiley),[116] (B) electric field induces gradient structure formation of lithium saponite nanoparticles (figure reproduced with permission from American Chemical Society),[87] (C) magnetic field induces directional alignment of magnetic nanoparticles (figure reproduced with permission from American Chemical Society),[19] (D) unidirectional freezing-assisted salting out (figure reproduced with permission from American Chemical Society),[81] and (E) mechanical training drives alignment of nanofibers along the stretch direction (figure reproduced with permission from American Chemical Society).[118]

etc.), 2D nanosheets or certain polysaccharide molecules along the direction of an applied electric or magnetic field to create various types of structured hydrogels.

Electric field control is an efficient method to create bionic ordered structured hydrogels due to its speedy and straightforward regulation.[52,135] By employing one or more electrodes, the application of an electric field arranges nanomaterials or disordered/ordered materials in a direction that coincides with the electric field. This process leads to the formation of structured hydrogels with bionic order.[52,111,136,137] It is crucial to note that the ordered arrangement can only be maintained for a brief period once the electric field is turned off. However, the structure can be fixed permanently with additional cross-linked polymerization using monomers or polymers.[52,85,87,135] For example, Tan *et al.* were inspired by living organisms' continual gradient structure and therefore employed charged nanoparticles to produce a concentration gradient between the electrodes under the influence of a direct electric current field. They also used a cross-linking method using polymers to create bionic hydrogels with a long-term fixed gradient structure (Fig. 3B).[87]

Electrophoretic migration of nanomaterials in high-intensity electric fields creates significant challenges. Magnetic field control, on the other hand, allows for the arrangement of samples in an uncontrolled, orderly manner, without size and shape constraints, compared to electric field control.[138,139] The inclusion of nanomaterials enables the magnetic field control of this construction strategy as these materials contain magnetically responsive electrons. When in a magnetic field, these electrons exhibit fast magnetic responsiveness.[140–142] Moreover, magnetic nanomaterials are introduced into the polymer matrix for cross-linking polymerization to form a hydrogel network. Even without magnetic field induction, the internal structure of the hydrogel shows an ordered arrangement.[19,110] For example, researchers had used magnetic nanoparticles to decorate rod-like cellulose nanocrystals, which, under the influence of a magnetic field, realize an ordered arrangement. As a result, the researchers were able to produce a bionic nanocomposite hydrogel with ordered microstructure, exhibiting remarkable mechanical properties (Fig. 3C).[19]

3.2.3. Directional freeze-casting. Directional freezing or ice-templating is a promising technique in advanced materials design and manufacture due to its ability to precisely control the structure and facilitate ease of expansion and wide range of applications.[10,62] This method involves freezing a polymer solution or its composite material capable of forming microcrystalline structures in a specific direction. Then, utilizing an ice template, the ice crystals formed by the solution undergo directional nucleation and growth, forming an ordered arrangement in a layered or porous micronetwork pore wall.[10,57,113,143–146] By changing the diameter size of the ice template, the pore structure's ordered arrangement size can be precisely adjusted.[62]

Freeze casting alone allows for the concentration and close packing of the polymer, forming an orderly arrangement of pore walls, but does not result in the strong aggregation and crystallization of polymer chains.[10,62] Therefore, it is necessary to combine with other procedures, such as cryopolymerization,[147–150] solvent replacement,[57,151,152] salting out[10,153] or annealing[62,108,113] to further form bionic hydrogels with an ordered array of layered or porous structures. The functions of these processes are mainly reflected in the following three aspects: (1) inducing microscopic gelation and stabilizing a network structure of ordered arranged microstructures; (2) promoting strong aggregation and crystallization of polymer chains leading to the formation of nanofiber networks; and (3) strengthening the ordered network structure of hydrogels at the nanoscale and molecular level across different length scales. For example, Yang *et al.* first subjected the PVA solution to unidirectional freezing to form a honeycomb pore structure and then induced PVA aggregation and crystallization to form an orderly arranged nanofiber network by assisted salt precipitation (Fig. 3D).[81] The synergistic effect of freeze-casting-assisted salt precipitation not only formed a bionic ordered structure but also improved the aggregation effect of the hydrogel network. This is essential for the preparation of bionic ordered structured hydrogels with excellent mechanical properties.[81]

3.2.4. Mechanical prestretching. Prestretching or mechanical training is a straightforward, effective, universal, and feasible method for creating bionic ordered structured hydrogel soft materials characterized by highly ordered aligned structures.[118,119] It is particularly suitable for relatively rigid polymers like 1D nanocelluloses, polysaccharides such as alginates and chitosan, and synthetic polymers because these materials are more sensitive to mechanical signals than flexible polymers.[20,56,126,154] The mechanical stretching strategy involves repeatedly training the randomly distributed hydrogel network structure to align along the stress direction and induce an ordered structure.[155–158] However, it is crucial to note that the nanocomposite may revert to an initially disordered state after a single pre-drawing period. To enhance the stability of the ordered structure, it is necessary for it to undergo further cross-linking polymerization of the polymer network in the later stage.[65,118,119,159] For example, a polyacrylamide hydrogel network was used to introduce rigid cellulose nanocrystals in the form of nanofibers. Mechanical training conditions caused the elastic deformation of the hydrogel network, thereby directing the nanofibers to align with the tensile direction to improve the ordered structure of the hydrogel (Fig. 3E).[118] The fracture toughness and anti-fatigue performance of hydrogels were enhanced, which could be applied to potential biomaterials and tissue engineering fields.[118]

3.2.5. Other construction methods. Four important methods for constructing bionic ordered structured hydrogels, namely self-assembly, external field control, directional freeze-casting and mechanical prestretching, were described above. Although these methods are currently the most common and widely used by researchers, it is still a challenge to construct complex hydrogels with bionic ordered structures from the molecular scale to the macroscopic scale; and there is still a need to develop new and simple manufacturing processes to construct bionic ordered structured hydrogels to be able to solve the above problems. The proposed new methods will also provide new opportunities and challenges for the development and transformation of this field of bionic ordered structured hydrogels. In recent years, novel construction methods such as microfluidics,[22] 3D printing,[23] electrostatic spinning,[25] welding[59] and phase separation[160] have been gradually developed.

Microfluidics is a technology capable of manipulating small quantities of fluids through microchannels at the micron level.[161] This technology utilizes injection of a precursor solution into a microchannel, where the solution is subdivided into droplets by applying an external pressure or electric field. These droplets then undergo cross-linking polymerization, ultimately resulting in the formation of ordered structured hydrogels.[22,160] Microfluidic technology can realize the accurate control of droplet particle size, flow speed and volume, so it has been widely concerned by researchers.[21,162,163] However, it still has certain limitations, such as fine processing and precise controlled assembly of complex components, which are urgent problems to be solved by microfluidic technology.[23,164] 3D printing technology has been developed by researchers to effectively solve the challenges now faced by microfluidics. It is the use of the shearing force of the injection process to make spontaneous orderly arrangement of nanomaterials in the pre-gel, thereby constructing a bionic ordered structured hydrogel.[23,24,93] Thus the obtained ordered structured hydrogels have a finer internal structure and excellent properties; and 3D printing technology is becoming increasingly popular for its ability to create complex internal structures from microns to centimeters in size.[165] Unfortunately, 3D printing technology also has the disadvantage of relatively low throughput and is not suitable for large-scale industrial production.[161] In order to solve the above-mentioned drawbacks and build a bionic ordered structured hydrogel with complex structures and functions, it also needs to be supplemented with other design processes based on 3D printing. For example, a series of synergistic approaches such as 3D printing-assisted self-assembly,[166] 3D printing-assisted magnetic field induction,[161] and 3D printing-assisted microfluidic technology[164] approaches were used to construct ordered structured hydrogels. It provides a new idea for constructing bionic ordered structured hydrogels with complex structures and diverse hierarchical structures and the parallel construction of two or more methods can realize large-scale production.

Electrostatic spinning is a technique in which polymer solutions are jet spun under the influence of an electrostatic field. It is used in the construction of nanometer or micron scale oriented or other arranged fiber structures, because it is able to form a relatively uniform fiber diameter and adjustable nanofiber structure.[25,26] Nonetheless, the bionic ordered structured hydrogels that are produced using the electrostatic spinning technique typically exhibit weak interfacial forces, which detrimentally impact their strength, toughness, and anti-fatigue performance.[167] Therefore, it is necessary to further combine with other construction methods such as welding technology to strengthen the ordered arrangement structure

inside the bionic hydrogel.[167] The welding technique involves the use of multiple hydrogel films having ordered arrangements for interfacial reconstruction to fabricate layered structures with various ordered orientations.[59,167] This method boosts the interfacial forces between the layers of the structure, improving the mechanical properties of the bionic ordered structured hydrogel.

Phase separation technology involves liquid–liquid phase separation triggered by external environmental conditions such as temperature and pressure coupled with supramolecular interactions. The resulting assembly yields bionic hydrogels with ordered arrangements *via* interactions.[160,168]

In conclusion, in addition to the four methods of self-assembly, external field control, directional freeze-casting and prestretching, which are relatively mature methods for constructing bionic ordered structured hydrogels, techniques such as welding, electrostatic spinning and phase separation are still worthy of further exploration by scientists. Progress in these methods opens new vistas for developing ordered structured hydrogels. In addition, some unusual methods such as UV induction, self-heating, *in situ* mineralization, *etc.* have been used to construct bionics-ordered structured hydrogels, as shown in Table 1.

4. The optimization mechanism of the bionic ordered structure of hydrogels

Traditional disordered hydrogels usually exhibit poor mechanical properties due to their loose cross-linked structure, low solid content and high moisture. Therefore, they cannot withstand high load and mechanical damage in practical applications, which greatly limit their application range.[10,169] As described in the previous sections, bio-inspired ordered structural hydrogels can greatly expand the space of parameters and become engineered soft materials with high strength, high toughness and modulus.[28,119,151,170] The mechanical properties of the ordered structured hydrogels are generally more excellent than the traditional disordered structure hydrogels (Fig. 4). It can be concluded that the space for scalable mechanical properties of this ordered structured hydrogel inspired by organisms is great. In this section, we will summarize the design principles of bionic ordered structure for hydrogel strengthening, toughening and anti-fatigue mechanism, and describe the tensile strength, Young's modulus, toughness, fatigue threshold and other parameters of different bionic ordered structured hydrogels through Table 2 to show the excellent mechanical properties of bionic ordered structured hydrogels. This also provides strong data support for the design of bionic ordered structured hydrogels with excellent mechanical properties.

4.1. Strengthening mechanism

Currently, while some hydrogels have a high degree of biocompatibility and water retention, they lack the necessary strength to withstand deformation caused by impacts, tension, compression, and other forces. This deficiency significantly limits the practical application of hydrogels.[60] In recent years, scientists have found inspiration from the ordered structures discovered in organisms and developed bionic ordered structured hydrogels to enhance their mechanical strength. The principle of this reinforcing mechanism is to increase the strength of the hydrogel by increasing its cross-linking density through the formation of ordered structures,[184,185] or to make it stress evenly by changing the topological structure of the hydrogel.[39,186]

Bionic ordered structured hydrogel characteristics can improve their mechanical properties by adjusting the degree of crosslinking.[112,184,185,187] This can be achieved by constructing ordered double network hydrogels,[20] introducing metal ions for coordination (Fig. 5A),[172] adding SiO_2 nanoparticles[188] and other methods. These techniques can increase the crosslinking density either directly or indirectly in the bionic ordered structured hydrogels. The degree of crosslinking can be calculated using the following formula based on the crosslinking density:

$$\rho = \nu/N_0 \quad (1)$$

where ν is the number of crosslinking units and N_0 is the total number of units contained in the polymer. According to formula (1), the crosslinking point is directly proportional to the crosslinking degree in a specific monomer. As a result of the increased crosslinking point, the crosslinking degree of the hydrogel network is also increased. This led to the formation of a denser hydrogel network, thereby increasing the mechanical strength.[112,172,189]

Despite the simplicity of improving the crosslinking degree, stress deformation during practical applications can cause a decrease in the crosslinking degree of hydrogels, which consequently affects their mechanical strength.[100,190] Additionally, an excessive degree of crosslinking can cause hydrogels to become more brittle and experience a loss of tensile strength.[184] Recently, there has been significant research on developing a uniform topological structure for hydrogels. Because of the disorderly arrangement of molecules within hydrogels, their internal strength can vary, causing them to break easily at the weakest point. This method mainly overcomes the above shortcomings of hydrogels by constructing bionic ordered structures, making the strength of each part of the hydrogel equal,[191] or enhancing the hydrogel strength from the crosslinking between hydrogel monomers.[100] Currently, two primary research directions exist. The first involves designing hydrogels capable of establishing the network direction. Drawing inspiration from mammalian cartilage tissue, hydrogels with a horizontal and synergistically ordered vertical network structure can be constructed. This unique bionic ordered structure uniformly distributes and coordinates forces exerted in all directions, avoiding easily breakable end plates and increasing strength.[36,60] Wyse Jackson and colleagues, for instance, discussed the bone tissue dispersion force principle, in which a double ordered layer worked collaboratively to withstand shear forces from different directions, while the inner collagen fiber was responsible for bearing compression forces. This bio-inspired ordered structure synchronized forces in all directions and enhanced structural strength as a result.[192]

These methods can result in significant anisotropy, with mechanical properties varying significantly between different

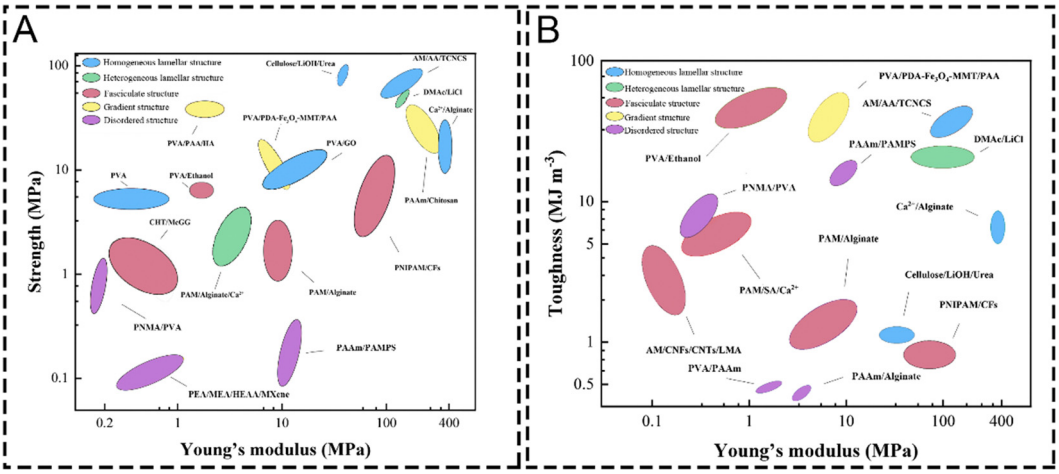

Fig. 4 Analysis of mechanical properties of various bionic ordered structured hydrogels and comparison with disordered structured hydrogels. According to the different strengths, Young's modulus and toughness values collected in Table 2, the (A) strength *versus* Young's modulus and (B) toughness *versus* Young's modulus of homogeneous lamellar structure (blue),[20,56,108,113,159,172] heterogeneous lamellar structure (green),[28,59] fasciculate structure (red),[44,77,114,151,174,175] gradient structure (yellow)[30,65,97] and disordered structure (purple)[180–183] hydrogels were compared by Ashby diagrams.

directions. Nevertheless, some specific fields require hydrogels to have uniform mechanical properties at all angles without any anisotropy, such as buffer type and omnidirectional force type applications.[62,100] Consequently, homogeneous network hydrogels have been developed (Fig. 5B). This approach entirely removes chemical bond connection-related uncertainty and randomness associated with crosslinking.[193–195] Designed cross-linked chemical bonds directly determine the mechanical strength of this fully connected hydrogel, thereby avoiding the effects of random crosslinking.[191] Takamasa and colleagues approached the issue from a large tetrahedron perspective. They designed hydrogel monomer groups to ensure uniformity of crosslinking sites in hydrogels and used links from tetrahedral apex groups to disperse forces through ordered structures.[100]

In summary, bionic ordered structures can effectively boost the hydrogel's mechanical strength. The structured pattern optimizes the hydrogel network's crosslinking, thus rectifying the limitations of traditional hydrogels.

4.2. Toughening mechanism

Toughness refers to how much energy materials can absorb during plastic deformation and fracture.[36] Traditional disordered hydrogels are typically not highly durable and struggle with effective energy dissipation when subjected to a specific area.[28,39] Inspired by biological tissues, researchers have discovered that adding oriented long-chain macromolecules as the skeleton can enhance the toughness of hydrogels, promote force dissipation, and create different ordered structures to optimize conduction and dissipation.[196]

The primary function of the toughening mechanism is to enhance the hydrogel's ductility and increase its energy dissipation capacity. The absence of a well-ordered structure in traditional hydrogels makes it challenging for powerful and weak bonds to collaborate, compromising their ability to efficiently absorb energy from broken bonds.[36,197] The ordered structure inspired by biology enables regular alignment of strong and weak bonds, leading to increased energy dissipation.[196,198,199] For this reason, directional macromolecules are required to be introduced into the hydrogel network to create bio-inspired ordered structures with strong and weak bond coordination.[39,59] The bionic ordered structure allows dipole–dipole interaction and inorganic–organic combination to act as energy sinks and efficiently dissipate external forces, resulting in significant improvement to hydrogel toughness (Fig. 5C).[59] For example, Yu and his colleagues achieved mechanical dissipation by adding lengthy hydroxyapatite chains, as discovered in a study.[36] Hydroxyl groups in hydroxyapatite formed strong hydrogen bonds with the hydrogel to absorb and dissipate external energy during fractures, thus improving material toughness.[36,39,196]

Apart from introducing oriented long-chain macromolecules to increase hydrogel dissipation, another method to enhance toughness is through transduction dissipation, which utilizes bionic ordered structures to transmit and dissipate stress. The specialized structure disperses the force from the point of application to a distant location and prevents premature breaking of the force point due to excessive energy.[46,189,190] By doing so, the amount of absorbed energy before the hydrogel breaks increases, resulting in improved toughness. Moreover, researchers have discovered that various types of bionic ordered structures possess distinctive methods for dispersing and transmitting energy.[28,39,190] For instance, the ordered fasciculate structure proves highly effective for transmitting and dissipating force within the internal tube bundle of hydrogels. Specifically, their directional tube bundles possess strong covalent bonds that allow the force to "travel" to farther regions from the point of contact, leading to greater energy absorption from broken weak bonds.[62,200] The fracture of the tube at the point of force effectively dissipates energy and significantly enhances the hydrogel's toughness.[36,46,62] In the ordered lamellar structure, the multi-layered structure with different layers effectively transmits force to various parts of the hydrogel through extrusion friction between the layers (Fig. 5D).[28,46]

Table 2 Components, optimization mechanism, tensile strength, Young's modulus, toughness, fatigue threshold, cycle and application of bionic ordered structured hydrogels

Components	Optimization mechanism	Parallel/vertical direction tensile strength (MPa)	Young's modulus (MPa)	Toughness (MJ m^{-3}/ MJ m^{-2})	Parallel/vertical direction fatigue threshold (kJ m^{-2})	Cycle	Application	Ref.
PVA/HA/gelatin/alginate	Strengthening, toughening, and anti-fatigue	23.5 ± 2.7	—	210 ± 13 MJ m^{-3}	10.5 ± 1.3	30 000	Bioremediation materials, actuators	10
PVA	Strengthening, anti-fatigue	8.4	—	—	0.77	5000	Impact resistant materials	167
PVA/MXene/Zn^{2+}	Strengthening, toughening	0.875	—	0.082 MJ m^{-3}	—	—	Sensors	57
PVA/ethanol	Strengthening, toughening, anti-fatigue	6.5	1.69	58.9 MJ m^{-3}	—	64 800	Sensors	151
PNDU/CNF/CNT	Strengthening, toughening, and anti-fatigue	0.093	0.023	0.193 MJ m^{-3}	0.187	2000	Sensors	171
AM/AA/TCNCS	Strengthening, toughening	56	152	42 MJ m^{-3}	—	—	Bioremediation materials	172
PVA	Strengthening, anti-fatigue	5.2/1.1	0.2	—	1.25/0.233	30 000	Bioremediation materials	56
PVA/PANa	Strengthening	7	—	—	—	—	Sensors	173
PAM/alginate/Ca^{2+}	Strengthening, toughening	1.3	0.5	0.00109 MJ m^{-2}	—	—	Bioremediation materials, actuators	28
PAAm/CNC	Strengthening, toughening, and anti-fatigue	—	0.0147	0.001 MJ m^{-2}	0.083	10 000	—	118
DMAc/LiCl	Strengthening, toughening	47	140	20 MJ m^{-3}	—	—	Bioremediation materials	59
PAAm/chitosan	Strengthen	25.6	218.2	—	—	—	Bioremediation materials	65
Cellulose/LiOH/urea	Strengthening, toughening	79.8	37.93	1.080 MJ m^{-3}	—	—	—	159
PVA	Strengthening, toughening, and anti-fatigue	2.5	—	0.116 MJ m^{-2}	1.34/0.034	1 000 000	Actuators	62
PVA/GO	Strengthening, toughening, and anti-fatigue	8.8	9.2	0.0857 MJ m^{-2}	1.567/1.539	30 000	Actuators, Impact resistant materials	108 and 113
PVA/CNF/DEL	Strengthening	4.1	—	—	—	—	Bioremediation materials, actuators, and sensors	119
BC	Strengthening, toughening	83	—	116.3 MJ m^{-3}	—	—	Bioremediation materials	39
PVA/AAM/alginate	Toughening, anti-fatigue	—	—	0.001 MJ m^{-2}	0.8	30 000	Bioremediation materials	37
PAM/SA/Ca^{2+}	Strengthening, toughening	1.65	0.27	5.75 MJ m^{-3}	—	—	Sensors	174
PVA/PVP/CNCs/Fe^{3+}	Strengthening, toughening, and anti-fatigue	2.1	—	8.9 ± 0.78 MJ m^{-3}	—	—	Sensors	170
AM/CNFs/CNTs/LMA	Strengthening, toughening, and anti-fatigue	—	0.1–0.25	3.6 MJ m^{-3}	0.106	2000	Sensors	175
TA/P(MAA-*co*-OEGMA)/Fe^{3+}	Strengthening, toughening, and anti-fatigue	1.27/0.28	—	2 MJ m^{-3}	—	—	Actuators	176
PVA/PDA-Fe_3O_4-MMT/PAA	Strengthening, toughening, and anti-fatigue	10.91 ± 0.62	9.21 ± 0.67	47.53 ± 5.64 MJ m^{-3}	1.359	10 000	Bioremediation materials	30
PVA/PAA/HA	Strengthening, toughening	38.9 ± 1.5	1.73 ± 0.06	—	—	—	Bioremediation materials	97
PAAS/PMA	Strengthening, toughening	5.6 ± 0.6	-	26.8 ± 3.1 MJ m^{-3}	—	—	Sensors	177
PAM/alginate	Strengthening, toughening	1.3	7.2	1.4 MJ m^{-3}	—	—	Bioremediation materials	44
SA/HAP/Ca^{2+}	Strengthening	67.8	670	—	—	—	Bioremediation materials	43
PNIPAM/CFs	Strengthening, toughening, and anti-fatigue	3.0 ± 0.3	74 ± 7.0	0.9 MJ m^{-3}	—	—	Actuators, sensors	114
CHT/MeGG	Strengthening	1	3	—	—	—	Bioremediation material	77
Ca^{2+}/Alginate	Strengthening, toughening	53.55 ± 0.53	342.44 ± 31.14	16.44 ± 0.99 MJ m^{-3}	—	—	Bioapplications	20
PHEA-API/PAM/alginate	Strengthening	0.8	3	—	—	—	Bioremediation materials	112

Table 2 (*continued*)

Components	Optimization mechanism	Parallel/vertical direction tensile strength (MPa)	Young's modulus (MPa)	Toughness (MJ m^{-3}/ MJ m^{-2})	Parallel/vertical direction fatigue threshold (kJ m^{-2})	Cycle	Application	Ref.
PVA/MXene	Strengthen	0.14/0.101	0.248/0.12	—	—	—	Sensors	81
NaAlg/GO	Strengthening, toughening	1215 ± 80	198.8 ± 6.5	36.7 ± 3.0 MJ m^{-3}	—	—	—	124
Betaine/AgNPs/ NaCl	Strengthening	12.04	25.9	—	—	—	Sensors	178
BC/LiOH/urea	Strengthening	14.3	38.9	—	—	—	—	179
Chitin fibers/ lobster membrane	Strengthening, toughening	23.36	0.23	24.98 MJ m^{-3}	—	—	Actuators	46
PVA/CNT	Strengthening, and anti-fatigue	4.5	—	—	1.467	—	Sensors	117

PVA: polyvinyl alcohol; HA: hyaluronic acid; GO: graphene oxide; PNDU: poly(NaSS-*co*-DMAEA-Q-*co*-UM); CNT: carbon nanotube; PAAm: polyacrylamide; CNC: cellulose nanocrystal; TCNCs: tunicate cellulose nanocrystals; AA: acrylic acid; AM: acrylamide; PANa: sodium phytate; LiCl: lithium chloride; DMAc: *N*,*N*-dimethylacetamide; CNF: cellulose nanofibrils; DEL: enzyme-hydrolyzed lignin; BC: bacterial cellulose; SA: sodium alginate; PVP: poly(vinylpyrrolidone); LMA: lauryl methacrylate; MMT: montmorillonite; poly(MAA-*co*-OEGMA): poly(methacrylic acid-*co*-oligo(ethylene glycol)methacrylate); TA: tannic acid; PAAS: sodium polyacrylate; MA: methyl acrylate; PNIPAM: poly(*N*-isopropylacrylamide); CFs: carbon fibers; CHT: cationic chitosan; GG: anionic gellan gum; PHEAAPI: poly(2-hydroxyethylaspartamide) modified with aminopropyl imidazole; NaAlg: sodium alginate; and AgNPs: silver nanoparticles.

The coordination of the strong layer and weak layer is akin to that of the strong and weak bond. The strong layer is responsible for transmitting the force to the weak layer, which, in turn, is responsible for dissipating the force.[20,59] For example, Wu and his colleagues designed a staggered multi-layer high-toughness hydrogel, inspired by the crayfish shell. The alternating arrangement of strong and weak layers contributed to a robust interaction that enabled the hydrogel to disperse force effectively and have strong impact toughness (Fig. 5E).[46] Gradient structures resemble layered structures and transmit force through ordered gradient holes or other gradient methods to prevent rupture caused by excessive force at a particular point.[90,92]

In summary, the ordered structure observed in bionic organisms plays a significant role in improving the toughness of hydrogels. This is primarily due to its ability to enhance the hydrogel's resistance to external forces.

4.3. Anti-fatigue mechanism

Currently, some hydrogels can withstand deformation under a single mechanical load cycle, but hydrogels are still susceptible to fatigue fracture under multi-cycle mechanical loading, which makes the long-term reliability of hydrogels for practical applications challenging.[201] In recent years, inspired by the ordered structure in biological tissues, scientists have proposed that the bionic ordered structure can improve the anti-fatigue properties of hydrogels.[10,113]

The design mechanism of anti-fatigue hydrogels is to allow fatigue cracks to encounter and destroy materials that are stronger than the amorphous polymer chains during growth. In other words, substances with high intrinsic fracture energy are used to prevent fatigue crack propagation of hydrogels.[8] Fatigue threshold (*i.e.*, the minimum fracture energy for crack extension to occur under cyclic loading) is the main parameter for assessing the resistance of hydrogel to fatigue crack extension.[37,171] Generally, fatigue threshold can be obtained by the pure shear crack fracture test, peeling test and single notch crack fracture test. Fatigue threshold (Γ, kJ m^{-2}) can be obtained using eqn (2):

$$dc/dN = AG^m \quad (2)$$

where dc/dN is the crack propagation per cycle, G is the energy release rate applied, *i.e.* the intercept with the x-coordinate, and A and m are the material constants. The energy release rate value (G) obtained by linear extrapolation is equal to the true fatigue threshold (Γ) of the hydrogel sample.[202,203] Therefore, ordered microcrystalline structure is introduced into the hydrogel network as a stronger substance than the amorphous polymer chain, which effectively prevents crack diffusion and improves its fatigue threshold.[10,37,204]

Biological tissues such as tendons, cartilages, and skeletal muscles show extraordinary anti-fatigue properties, which may depend on the highly ordered and partially crystalline structure of collagen fibers inherent in biological tissues.[8,10] Based on this, scientists often improve anti-fatigue properties of bionic hydrogels by constructing the ordered structure of bionic hydrogels with polymers that can form partially crystalline structures internally, using methods such as directional freeze-casting and prestretching.[10,56,62,65,175] However, despite the enhanced anti-fatigue properties of bionic ordered structured hydrogels, it is difficult for pure polymer networks to sustain the ordered oriented microcrystalline structure, and the enhanced anti-fatigue properties are not durable, thus limiting the practical application of bionic hydrogels. To better stabilize the ordered structure and enhance the anti-fatigue properties of bionic hydrogels, researchers typically integrate nanocrystal domains or nanofibers into the polymer network to make the ordered structure of bionic hydrogel networks more dense.[8,37,171] For example, scientists typically introduced nanocrystal domains into polymer networks by means of the salting out[10,204] or annealing process[8,37,62,167] to increase the crystallinity within the hydrogel network, achieving dense and structurally fixed

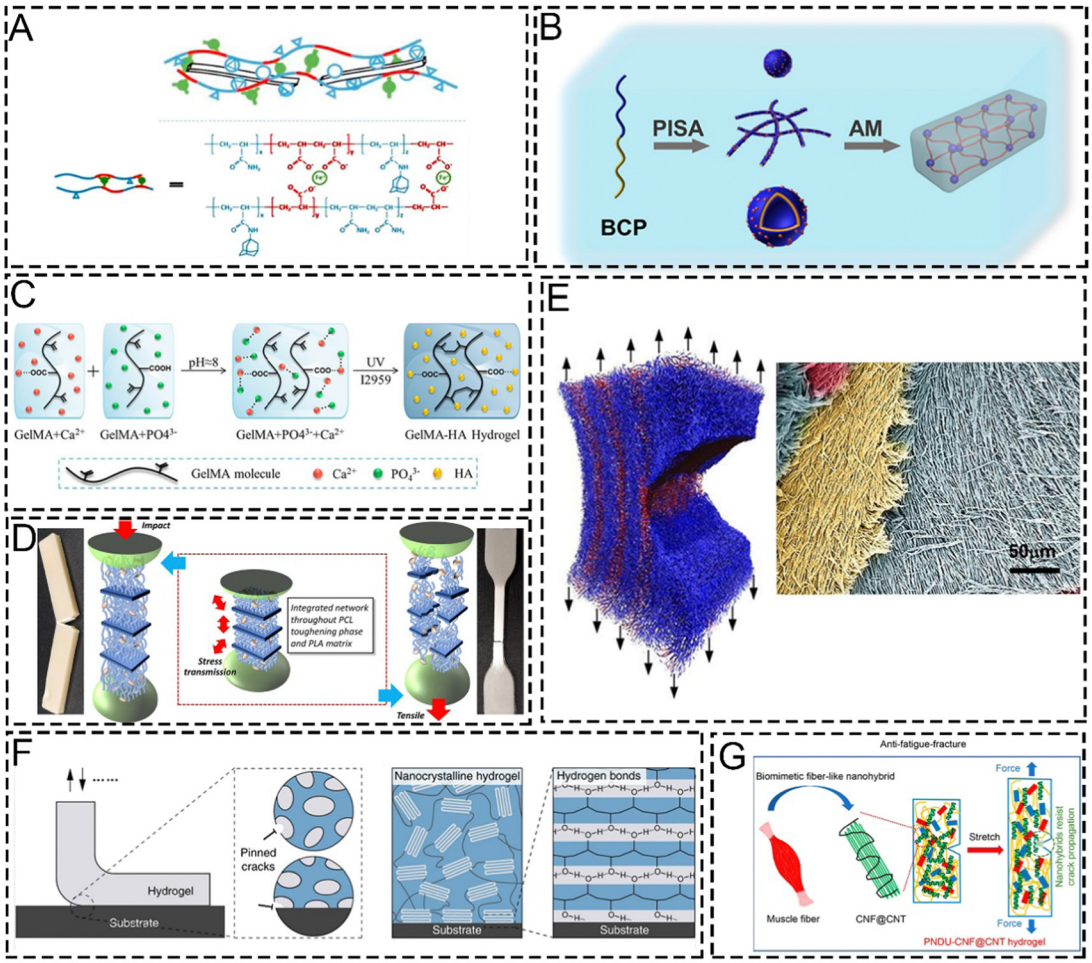

Fig. 5 The bionic ordered structured hydrogel improves its strength by (A) the increase of crosslinking points through the coordination of metal ions (figure reproduced with permission from Elsevier)[172] and (B) the formation of homogeneous network hydrogel (figure reproduced with permission from American Chemical Society),[205] improves its toughening by (C) introducing long chain macromolecules (figure reproduced with permission from American Chemical Society),[206] (D) building a special dual network lamellar structure (figure reproduced with permission from American Chemical Society)[207] and (E) constructing lamellar ordered structures to achieve force dispersion (figure reproduced with permission from Elsevier),[46] and improves its anti-fatigue by (F) the growth of nanocrystal domains to fix ordered structure (figure reproduced with permission from Nature)[37] and (G) fixing the crack and preventing crack growth through the ordered arrangement nanofibers (figure reproduced with permission from American Chemical Society).[171]

polymer networks. Thus, the fatigue threshold of bionic ordered structured hydrogel can be improved and the anti-fatigue properties can be enhanced (Fig. 5F).[10] However, this method of fixing the ordered structure of the bionic hydrogel by introducing nanocrystalline domains suffers from limitations in the selection of materials and high crystallinity that reduces the water content inside the bionic hydrogel.[56] Therefore, the researchers also proposed that by introducing nanofibers into the polymer network for tensile orientation, breaking the nanofibers requires higher energy than breaking the polymer chains, which could effectively fix the crack expansion and play an important role in the enhanced anti-fatigue properties of the bionic hydrogel (Fig. 5G).[118]

Although the bionic ordered structured hydrogel can improve the fatigue threshold along the direction of ordered structures, a lower fatigue threshold still remains perpendicular to the direction of ordered arrangement.[108,113] Scientists have recently developed 2D layered ordered structures for constructing bionic hydrogels, leveraging a bidirectional freeze-assisted annealing technique to induce the nucleation and growth of ice crystals along the temperature gradient, thereby generating a porous and layered ordered structure. The resulting hydrogels exhibit high fatigue thresholds, both parallel and perpendicular to the direction of the ordered arrangement, showcasing exceptional anti-fatigue properties.[108,113] The exploration of this technique offers a new approach for enhancing the anti-fatigue properties of bionic ordered structures and inspires the development of novel applications.

In summary, the introduction of nanocrystal domains or nanofibers into the polymer network increases its resistance to fracture, compared to amorphous polymer chains. Therefore, the ordered structure construction plays a vital role in improving the anti-fatigue properties of bionic ordered structured hydrogels.

5. Applications

Compared to artificial materials, biological tissues possess unparalleled mechanical properties due to their highly organized structure. This concept has inspired the development of bionic ordered structured hydrogels, which possess high strength, toughness, and anti-fatigue properties, and have become essential engineering materials in many fields. This section will focus on several typical applications of bionic ordered structured hydrogels, including their use in sensors, bioremediation materials, actuators, and impact resistant materials. Furthermore, we will clarify the unique role that bionic ordered structures play in these applications.

5.1. Sensors

Hydrogel sensors possess the ability to sensitively and selectively detect changes in the chemical and physical environments by undergoing volume phase transitions *via* water absorption or loss.[208,209] Unfortunately, many sensors of this type experience limited tensile capacity, low toughness, and rapid signal degradation when exposed to long-term cyclic strain.[210,211] Therefore, the ordered structure of biological tissues serves as inspiration for the design of bionic ordered structured hydrogel sensors. The ordered structure of hydrogels enables sensors to exhibit highly sensitive, repeatable, and stable changes in resistance when subjected to mechanical deformation, which makes them ideal for monitoring human movement[57,81,171,212] and delivering important information.[170,213,214]

The advancement of technology along with the progress in artificial intelligence has drawn a significant amount of attention to the use of sensors as a prime option for monitoring human bodily health. Human motion amplitude and frequency are indicators of the body's motor function and physiological state. These indicators offer crucial clinical information for disease diagnosis and medical treatment.[215] Bionic ordered structured hydrogel sensors are commonly employed to monitor human motion through the mechanical alteration of the hydrogel. This alteration enables the acquisition of amplitudes and frequencies of movement ranging from the joint to muscle level. Bionic ordered structured hydrogel sensors are typically affixed firmly to body joints, including knee, elbow, finger joints, *etc.*, to detect significant motions of the human body. The bending and straightening of joints deform the hydrogel, which in turn generates an electrical signal.[31,57,81,171,216] An instance of this included attaching bionic ordered structured hydrogel sensors to the knee joint of the human body. The hydrogel was deformed by the changing state of the knee from extension to bending, so that after several bending and extension of the knee, the resistance signal output from the sensor increased accordingly and showed a periodic recovery (Fig. 6A).[171] Moreover, the bionic ordered structured hydrogel sensors have a stable and high sensitivity range that make them capable of detecting not only significant joint movements but also minor muscle movements. Small muscle movements such as smiles, frowns, heart rate, pulse beats, vocal cord vibrations, *etc.* are monitored by attaching bionic ordered structured hydrogel sensors to the face, wrist, neck, *etc.*[57,175,213] For example, bionic ordered structured hydrogel sensors attached to the forehead, corners of the eyes, or cheeks could detect human facial expressions by sensing muscle movements that were imperceptible or indistinguishable to the naked eye (Fig. 6B).[174] Furthermore, bionic ordered structured hydrogel sensors were placed on the human wrist to monitor pulse activity. By comparing pulse changes before and after exercising, the amplitude and frequency of the resistance output signal relative to the sensor were significantly enhanced post-exercise (Fig. 6C).[170] In summary, the bionic ordered structured hydrogel sensors exhibit both high strain sensitivity and durability, which is verified by stable and clear electrical signals transmitted. This makes them useful for detecting various human movements as they switch from large to small strains.

A sensor is a detection device that converts the information received into an electrical or other signal output.[217] Currently, sensors transmit information primarily through techniques such as speech recognition and intelligent coding. In order to prevent the risks associated with delays, inaccuracies, or interruptions during the information delivery process, bionic ordered structured hydrogel sensors with high sensitivity and long-term stability are necessary. Speech recognition involves obtaining resistance signals *via* vocal cord vibrations. Since different words entail different muscle movements (Fig. 6D),[218] information may be recognized based on the amplitude and waveform of the generated signal.[57,175] The speech recognition feature of the sensor is anticipated to provide voice communication for individuals with speech disabilities. Intelligent coding pertains to the use of the International Morse Code, a system that uses a combination of dots and dashes to represent letters and numbers and enables secure communication through encryption and decryption.[219] The key characteristic of Morse code lies in its capability to remotely transmit and modify information through the use of body movements.[81,153,173] As an illustration, a bionic ordered structured hydrogel sensor was affixed to a human knuckle. This sensor produced sequences of dots and dashes that correspond to different letters or numbers, depending on the extent of finger flexion. The information that was transmitted was evaluated based on the Morse code's coding principles (Fig. 6E).[153]

In summary, the bionic hydrogel sensor with an ordered structure provides high sensitivity over a broad range of strains and durability under long-term cyclic mechanical loading, making it a promising technology for various applications, including human health detection, motion state recognition and information delivery.

5.2. Bioremediation material

Traditional hydrogels as bioremediation materials often have disadvantages such as low strength, poor adhesion and poor biocompatibility.[220–222] However, the hydrogels prepared using bionic ordered structures can effectively enhance these properties, especially high strength and toughness.[223] Therefore, bionic ordered structured hydrogels can be used as excellent bioremediation materials for sutures,[39,224] bioadhesives,[225–228] wound dressing[162,229–231] and implants.

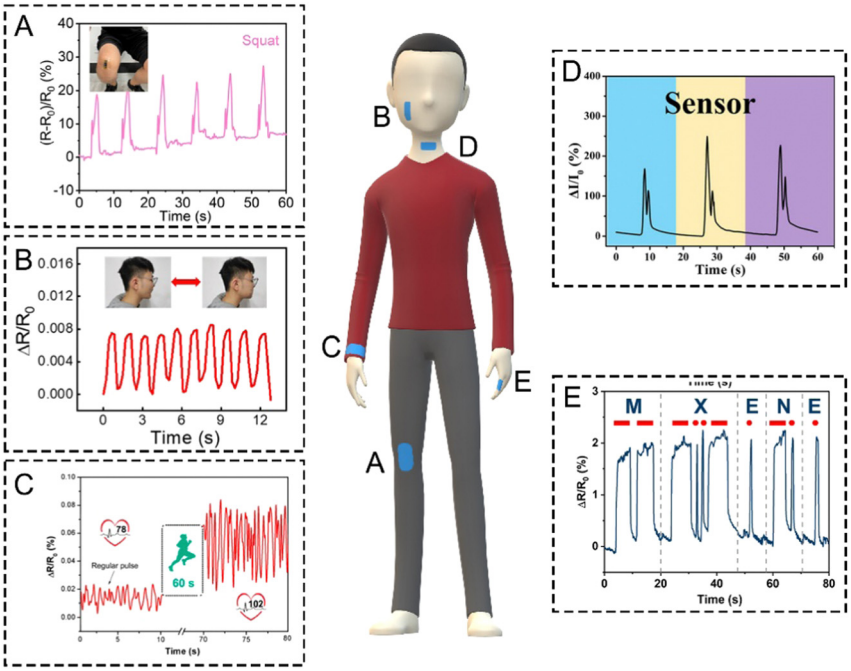

Fig. 6 Application of a bionic ordered structured hydrogel sensor for human movement detection and information delivery. Electrical signal response of the sensor to (A) knee flexion (figure reproduced with permission from American Chemical Society),[171] (B) cheek puckering (figure reproduced with permission from American Chemical Society),[174] (C) pulse before and after motion (figure reproduced with permission from American Chemical Society),[170] (D) speech recognition (figure reproduced with permission from American Chemical Society)[218] and (E) Morse code (figure reproduced with permission from American Chemical Society).[153]

Sutures serve as crucial bioremediation materials and have a wide range of applications in wound healing and surgical procedures. Traditional sutures, including plastic, biologically derived protein and metallic sutures, often exhibit poor elasticity and tensile strength.[232] Conversely, bionic ordered structured hydrogel sutures with plastic mechanical properties and biocompatibility can reduce tissue trauma and promote wound healing. Additionally, *in vitro* trials have indicated that bionic ordered structured hydrogel sutures outperform typical sutures in the protection and repair of wounds.[39,224] By imitating the ordered structures in living organisms, such as the spiral structure of lotus fibers and tendon endotenon sheath, the bionic ordered structured hydrogel sutures are prepared with not only excellent tensile strength, but also good flexibility and lubricity. Thanks to these advantages, the wound could be repaired better and secondary damage to the skin tissue caused by stiff sutures could be prevented.[39,224,232] For example, when the skin was stretched by an external force, the sutures were stretched without cutting into the skin, which prevented injury to the wound and promoted healing (Fig. 7A).[39]

A bioadhesive can be used as a substitute for suture, which is widely used in clinics. However, existing bioadhesives are not yet able to meet the standards of an ideal bioadhesive in terms of properties. They are not only cytotoxic but also exhibit poor adhesion strength, mechanical properties and others.[233,234] The bionic ordered structured hydrogels can effectively improve these properties and become excellent bioadhesives. Taking inspiration from the adhesion mechanism of mussel proteins to human tissues, bionic ordered structured hydrogel adhesives have been prepared. The ordered structure renders the hydrogel to have better strength and toughness, so that the hydrogel adhesives can better adhere to the tissue and maintain stability. Furthermore, because the hydrogel is an absorbent, it can rapidly absorb water from the tissue surface, resulting in fast, strong, durable, and robust adhesion.[226] This also allowed the bionic ordered structured hydrogel adhesive to remain stable and the hydrogel's appropriate swelling rate gave it the basic requirements for durable adhesion without causing pressure on the tissue, thus better facilitating wound healing. These bionic ordered structured hydrogel dressings also had excellent biocompatibility, reducing immune responses and reducing cytotoxicity.[225,226,233,235] Based on the above advantages of bionic ordered structured hydrogel adhesives, they had a wide range of applications, not only for *in vitro* wound healing but also for *in vivo* tissues such as in the stomach.[227]

Wound dressing is a common material used for wound repair, such as gauze, cotton wool *etc.* However, their treatment may be slow, and during the debridement process, it may tear new tissue.[236] Therefore, inspired by embryonic wound healing and *staphylococcal* defense strategies,[229,236,237] researchers have prepared a variety of bionic ordered structured hydrogels for wound dressing. The bionic ordered structure enhanced the mechanical properties of the bionic ordered structured hydrogel dressing, thus enabling it to resist loading in order to prevent mechanical disturbance of the wound by the environment, *etc.* It also improved the stability of the dressing, thus providing continuous protection and treatment.[229,236,238] For example, bionic ordered structured hydrogels can be used as

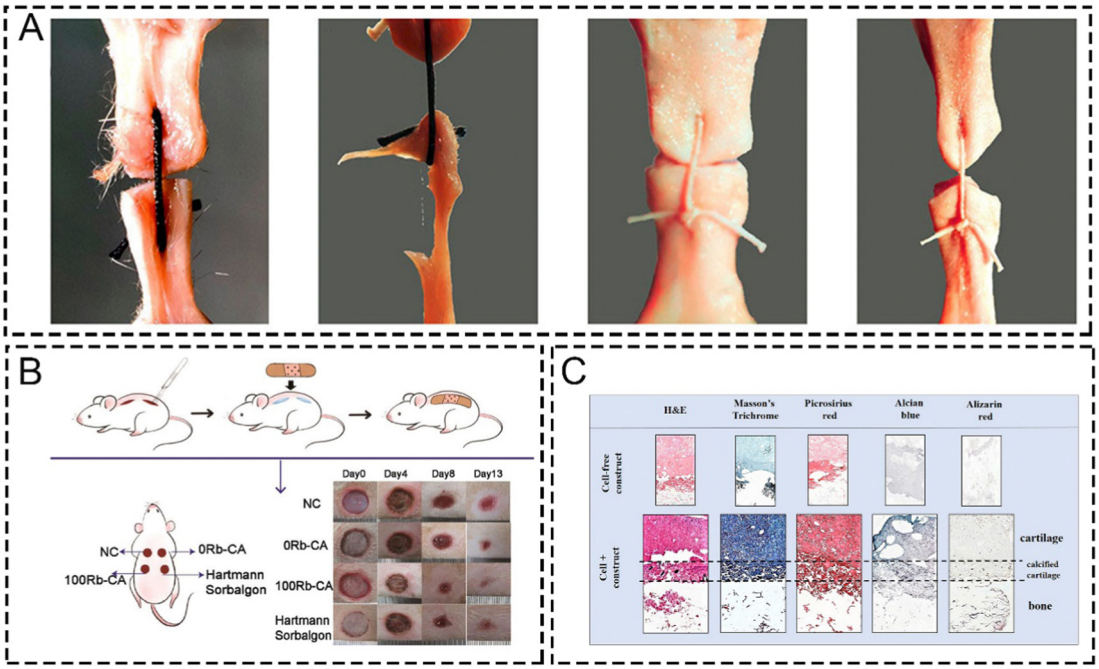

Fig. 7 Bionic ordered structured hydrogel bioremediation materials as (A) biological sutures are used to suture rat skin *in vitro* with reduced tissue damage compared with conventional sutures (figure reproduced with permission from American Chemical Society),[39] (B) wound dressings are used for rat wound repair to quickly promote wound healing (figure reproduced with permission from American Chemical Society),[239] and (C) implants replace cartilage tissue to promote tissue cell proliferation (figure reproduced with permission from Elsevier).[89]

dressings to provide stable protection for external wounds in rats, while speeding up wound healing (Fig. 7B).[239] It can be used not only for general wounds but also for oral and chronic wounds, and it functions as an alveolar dressing. For instance, the bionic ordered structure could effectively improve the strength of the hydrogel dressing and tensile resistance to swelling. It could adapt to the oral environment and be used as an alveolar dressing.[238] Moreover, there was a bionic hydrogel microneedle dressing with a special shape inspired by shark teeth that could be used for chronic wound recovery. Its flat and sloping structure gave the hydrogel dressing excellent mechanical properties, allowing it to penetrate the skin easily and maintain stable adhesion during the long-term recovery of chronic wounds.[162]

In addition, bionic ordered structured hydrogels are used as implants for bioremediation materials. The hydrogel is considered an excellent alternative to human tissues due to its high water content, flexibility, and excellent biocompatibility. Nevertheless, most hydrogels lack an ordered and stable structure that is capable of resisting fatigue and fracture, which limits their use in medical implants.[240,241] Bionic ordered structured hydrogels are able to support thousands of times the weight of the human body and remain highly resilient over millions of mechanical load cycles due to their excellent mechanical properties. Therefore, they can be used as human tissue implants for the repair and regeneration of soft tissues. The skeleton in the human body is an important structure that supports the body and also connects muscles, tendons, ligaments and other tissues and plays an important role in protecting internal organs. However, in some specific cases, it can be damaged including the surrounding soft tissues and vital organs, thus seriously affecting people's quality of life.[37] Bionic ordered structured hydrogels can be used as multilayered scaffolds to mimic the multilayered osteochondral structure to meet the heterogeneity and layered structure of natural osteochondral tissue or to create artificial ligaments that resemble the oriented structure of human ligaments. As a human medical implant, it provides effective mechanical support and developmental guidance for tissue growth and new tissue formation.[89,117] For example, the multi-layer gradient structure mimicking bones was implanted into the tissue as an implant for the repair and replacement of cartilage. Following several days of culture, histological examination indicated significant proliferation of somatic cells (Fig. 7C).[89] Thus, it is proved that the bionic ordered structured hydrogel could be used as an osteochondral scaffold, using its porous and continuous gradient structure to guide the effectiveness of chondrocyte differentiation and proliferation.[89] In addition to bone tissue engineering, a bionic ordered structured hydrogel with a triple network structure could also be implanted under the skin for full skin repair.[242] This bionic ordered structured hydrogel therefore offers a new solution for the development of medical implants due to its excellent durability and similar properties to the extracellular matrix.

5.3. Actuators

An actuator is a device that converts external environmental energy (electricity, light, heat, *etc.*) into mechanical work.[243–246] Owing to the inferior mechanical properties of hydrogels, actuators face challenges in responding promptly and sensitively to

external stimuli, while exhibiting limited force output.[219,247,248] Therefore, inspired by the structure of biological soft tissue, bionic ordered structured hydrogel actuators with excellent mechanical properties are prepared. These actuators, which can be used for both simple morphological transformation and complex position movement, have received extensive attention in applications such as intelligent grippers,[90,95] cargo transportation,[249,250] valve systems,[87,90] and soft robots.[113,249]

The unique bionic ordered structure design introduces apparent anisotropy to the hydrogel, leading to substantial differences in mechanical properties in different directions.[27,37] By utilizing this feature, bionic ordered structured hydrogel actuators can undergo simple morphological transformations such as bending, folding, and torsion in response to external stimuli as a result of non-uniform deformation of the hydrogel.[75,90,95,176] An exemplary case was a muscle-like ordered-structured hydrogel that could shrink by 48.2% along the stretching direction within 1 s of heating, albeit only 11% in the vertical direction, indicating anisotropic shrinkage ability. This ordered structure design delivered not only an ultrarapid shape change rate but also excellent shape programmability to the hydrogel actuator. It had the potential to simulate the motion characteristics of living organisms in nature, including the flight and landing patterns of birds, under the influence of external stimuli (Fig. 8A).[176] The bionic ordered structured hydrogel actuator is well suited for intelligent grippers, cargo transportation, and valve systems, thanks to its distinct morphological transformation properties. Specifically, the hydrogel-based smart gripper can achieve a firm hold and release of the target object by transforming from bending to stretching.[90,250] Moreover, the exceptional mechanical strength achieved by the hydrogel actuator, which arises from its bionic ordered structure, is likely to facilitate the lifting and transportation of heavy goods (Fig. 8B).[249,251] Furthermore, owing to the desirable non-shrinkage and excellent reversibility features associated with the bionic ordered structured hydrogel actuator, it may serve as an effective microfluidic valve.[252] For example, when a bionic gradient hydrogel actuator that was responsive to temperature was integrated into a temperature-controlled microfluidic switch, it caused asymmetric bending of the hydrogel, driving the switch open when the temperature surpassed the low critical transition temperature (LCST). Subsequently, the switch could be closed by reducing the temperature below LCST (Fig. 8C).[87]

However, after years of development, researchers are no longer limited to making bionic ordered structured hydrogel actuators for simple morphological transformation, but further for the movement of complex positions, including swimming, crawling, walking,[113,249,252] and can even help soft robots perform more advanced tasks through machine learning, including shape detection, touch recognition and other functionalities.[253,254] As a result, the application of such actuators in soft robots has gained increasing attention. The programmable and deformable nature of hydrogels allows bionic ordered structured hydrogel actuators to convert their own deformation into motion when exposed to external stimuli, enabling a diverse range of driving behaviors.[95,255] As an example, a radiation-responsive ordered hydrogel actuator could contract rapidly, imitating the swimming motion of jellyfish, and guide elastic tentacles to paddle water (Fig. 8D).[252] However, radiation-responsive ordered hydrogel brakes have the disadvantage of being unable to adapt to fluctuations in external conditions and can only achieve one type of mechanical movement. However, machine learning can assist soft robots in accomplishing more complex tasks.[256,257] As an example, when a flexible fiber-optic curvature sensor combined with pressure and curvature data, multi-mode IP facilitated the accuracy of recognition and enabled more advanced tasks to be performed.[258]

In summary, the controllable deformation degree, fast response/recovery speed, and large output force bestowed upon the actuator by the bionic ordered structured hydrogel demonstrate great potential for a wide range of extended applications, including intelligent grippers, cargo transportation, valve systems, and soft robots.

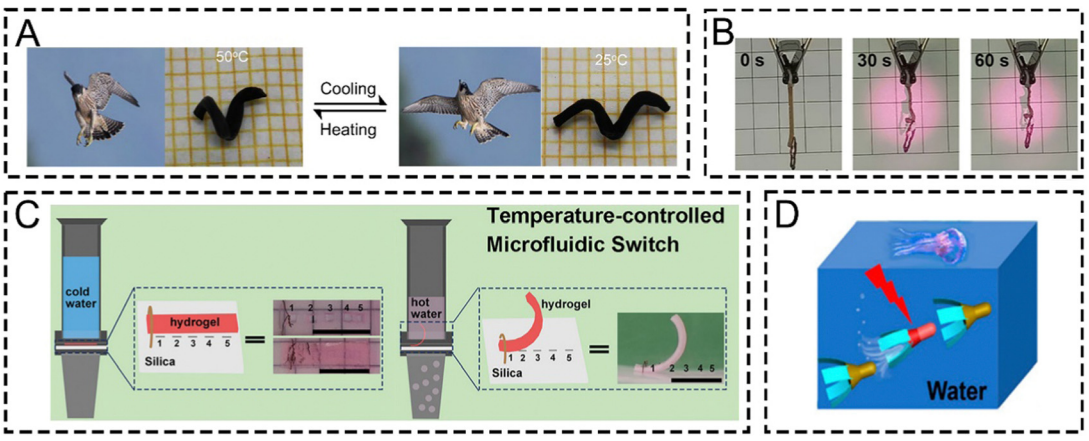

Fig. 8 The applications of a bionic ordered structured hydrogel actuator in (A) simulating the shape of a bird's flight and landing (figure reproduced with permission from American Chemical Society),[176] (B) lifting of cargo (figure reproduced with permission from American Chemical Society),[251] (C) closing and opening of a microfluidic switch (figure reproduced with permission from American Chemical Society),[87] and (D) imitating the swimming of jellyfish (figure reproduced with permission from American Chemical Society).[252]

5.4. Impact resistant materials

Impact resistant materials can act as a crucial protective barrier, ensuring the safety of our lives. With broad applications in the automotive industry, aerospace, military and other fields, they have immense application potential.[113,259] Despite ongoing research, designing hydrogel materials that retain sufficient strength under both quasi-static and impact loads remains a significant challenge. Natural organisms, such as shells, lobsters, and mantis shrimp, exhibit unique impact resistance through interlayer interactions that act to dissipate stress along both the plane and transverse directions.[108,260,261] The unique structure and mechanical relationship of these organisms have inspired the development of bionic ordered structured hydrogels.

Bionic ordered structured hydrogels offer the unique benefits of high-water content and flexibility, typical of hydrogels. At the same time, they exhibit remarkably high impact resistance, mechanical strength, and toughness. Therefore, they are expected to become flexible impact resistant materials to resist external shocks in many application scenarios. Bionic ordered structured hydrogel materials can enhance their impact resistance through the use of ordered structure hierarchies. These hierarchies achieve rapid absorption and dissipation of impact energy through the coordinated regulation of structure and interlayer interaction forces.[108,262–264] To provide an illustration, a bionic lamellar structure hydrogel inspired by the hierarchical lower abdomen structure of lobsters exhibited high impact resistance, a unique achievement for traditional hydrogel-based soft materials. Upon impacting with high-strength projectiles, the bionic lamellar structure hydrogel demonstrated notable resistance. Its surface remained unbroken and it induced considerable deformation to produce a rebound effect on the projectile. The improvement in the hydrogel's ballistic energy absorption and dissipation can be attributed to the strong interfacial interaction of the nanocrystal domain with the structural layer.[108]

The production of bionic ordered structured hydrogels offers promising opportunities to create cost-effective and long-lasting soft materials, widely applicable to everyday life. They can serve as protective components in various cases such as helmets, protectors, vehicle casings, bulletproof vests, armor, and more.

6. Conclusions and outlook

In this review, we provide the development of structure types and design strategies of bionic ordered structured hydrogels in recent years to develop hydrogel mechanical properties and mechanical indexes suitable for various applications. Inspired by the specific structures in different organisms of nature, this paper summarizes the common structural types of bionic ordered structured hydrogels, including the lamellar structure, fasciculate structure, gradient structure and other structures. Some traditional disordered structure hydrogels possess poor tensile properties, high brittleness, low flexibility, easy to occur fatigue fracture, poor self-recovery performance, *etc.*, which make it difficult to maintain the ductility, flexibility and stability in the application process. To overcome these challenges, researchers prepared bionic ordered structured hydrogels to improve the strength, toughness, and anti-fatigue performance of hydrogels through self-assembly, external field control, directional freeze-casting, and prestretching, which are more mature and common construction methods, or some other novel construction methods. With their superior mechanical properties, bionic ordered structured hydrogels can find broad applications in sensors, bioremediation materials, actuators, and other fields. The summary in this review of specific structures in different organisms and the design strategies for bionic ordered structures offers a valuable reference for the preparation of bionics and advanced engineering materials.

Despite being a promising area of research, current bionic ordered structured hydrogels still face several challenges that must be addressed. The most advanced construction method still requires refinement due to various limitations, including unsuitability for industrial mass production, inadequate precision for ordered structures, energy inefficiencies during preparation, limited availability of environmentally friendly materials, and high costs, among others. Additionally, the preparation of hydrogels with complex structures across different scales is still a significant challenge, often necessitating intricate design strategies. There remains significant potential for further exploration of new methods to construct bionic ordered structured hydrogels. Nonetheless, we anticipate that bionic ordered structured hydrogels will be instrumental in wearable and implantable bioelectronics, tissue engineering, biomedicine, and other emerging fields in the future.

Author contributions

Writing – original draft: Yanyan Wang and Xinyu Jiang; conceptualization: Xusheng Li, Kexin Ding and Xianrui Liu; investigation: Bin Huang and Junjie Ding; software: Keyu Qu, Wenzhi Sun and Zhongxin Xue; funding acquisition: Zhongxin Xue and Wenlong Xu; project administration, and writing – review and editing and supervision: Wenlong Xu.

Conflicts of interest

The authors declare no conflict of interest.

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