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Bioinspired Adaptive Gel Materials with Synergistic Heterostructures

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Abstract In nature, many biological soft tissues with synergistic heterostructures, such as sea cucumbers, skeletal muscles and cartilages, exhibit high functionality to adapt to complex environments. In artificial soft materials, hydrogels are similar to biological soft tissues due to the unique integration of "soft and wet" properties and elastic characteristics. However, currently hydrogel materials lack their necessary adaptability, including narrow working temperature windows and uncontrollable mechanics, thus restrict their engineering application in complex environments. Inspired by abovementioned biological soft tissues, researchers have increasingly developed heterostructural gel materials as functional soft materials with high adaptability to various mechanical and environmental conditions. This article summarizes our recent work on high-performance adaptive gel materials with synergistic heterostructures, including the critical design criteria and the state-of-the-art fabrication strategies of our gel materials. The functional adaptation properties of these heterostructural gel materials are also presented in details, including temperature, wettability, mechanical and shape adaption.

Keywords Bioinspired materials; Adaptive gels; Hydrogels; Mechanical strength; Shape memory

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INTRODUCTION

As one kind of the most important soft materials, hydrogel materials present three-dimensional (3D) crosslinked networks that consist of hydrophilic polymers and large amounts of water[1–4]. Owing to their unique compositional and structural similarities to the natural biological soft tissues and excellent elastic characteristics, hydrogels have attracted considerable attentions since their discovery[5, 6]. Up to now, hydrogel materials have been widely used in diverse applications fields, such as material science, electronic engineering, biochemical and biomedical areas. For example, they can act as actuators and sensors for reversible movement and control of soft robots[7–10], containers for drug delivery[11–13], or serve as 3D scaffolds for tissue engineering[14, 15].

In 1894, the word "hydrogel" was first coined to describe a colloidal gel of inorganic salts[16]. Around 1960, researchers first gave the scientific definition of hydrogel in the scientific literature, *i.e.* water-swollen crosslinked macromolecular networks[17, 18]. In the following three decades, the understanding of hydrogel materials remained relatively simple. During this period, the hydrogel processing was mainly based on covalent polymer networks derived from simple hydrophilic monomers and crosslinkers. In the 1960s, these hydrogels with simple covalent polymer networks were prepared by chain-addition reactions, mostly employing acrylamide (AM) or hydroxyalkyl methacrylate (HEMA) as the water-soluble monomer and *N*,*N*′-methylenebisacrylamide (Bis) as crosslinkers[19–21].

During the last three decades of the twentieth century, the environmentally responsive polymers were introduced into the scope of hydrogel materials[22–24]. At that time, a significant body of hydrogel research has focused on the responsive covalent polymer network under environmental changes, such as pH and temperature. For instance, poly(*N*-isopropylacrylamide) (PNIPAM) as a typical temperature responsive polymer is extensively studied. At a temperature above the lower critical solution temperature (LCST), the collapse of PNIPAM network causes the corresponding changes of transparency, swelling degree and mechanical properties of hydrogels[24]. However, some intrinsic drawbacks of conventional covalent polymer networks during this period limit the further application of hydrogels based on such structures. For example, these conventional synthetic hydrogels are inherently soft and brittle due to the single polymer network structure. In addition, the high swelling of such covalent polymer networks in water leads to the instable of hydrogel network structures, reducing the mechanical strength of hydrogels. Therefore, there is an unprecedented demand for the new hydrogels with high mechanical performance[25].

Consequently, the research focus towards hydrogel science is quickly shifting from conventional narrow networks to high-strength and tough networks obtained by optimizing

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polymer network structures and compositions. Since the early 2000s, many kinds of hydrogel polymer network systems with significant enhancements of mechanical performance over their conventional counterparts have been speedily developed by intensive research (Fig. 1). Milestones in the developments of high-strength and tough hydrogels include that Haraguchi *et al.* reported the nanocomposite hydrogels[26, 27], and Gong *et al.* reported the mechanically strong double-network hydrogel[28], and Suo *et al.* discovered the highly stretchable and tough hydrogels composed by hybrid crosslinking network[29], together with ultrastiff mineralized hydrogels in 2017[30]. The mechanical strength of these strong hydrogels may reach or even exceed that of biological soft tissues. Furthermore, functional hydrogel networks have also been promoted over the past decade. The typical examples include self-healing supramolecular hydrogels[31], non-swellable topological hydrogels[32], and nanocomposite hydrogels with anisotropic mechanical properties[33]. These works all together provide the general design criteria for preparing high strength and tough hydrogels.

Despite these achievements, the existing hydrogels with high mechanical performance are generally based on the single phasic hydrophilic polymer networks, whereas their lack of adaptive features still restricts their applications in complex environments. For instance, water as dispersion solvents in polymer networks inevitably freezes at subzero temperatures, thereby leading to hydrogels losing their original mechanical properties, *i.e.* elasticity and toughness. Moreover, although hydrogels with strong homogenous polymer network structures can achieve impressive mechanical strength, switchable mechanics and anisotropic mechanical properties are difficult to realize with such strong hydrogels. Additionally, unlike some biological tissues, such as muscles and cartilages, such strong hydrogel network also lacks necessary control ability of shape changing in complex environments. Therefore, a fundamental design principle together with innovative strategy for fabricating functional polymer network is of critical importance to develop next-generation adaptive gel materials.

In nature, functional adaptation of biological tissues stems from synergistic coexistence of heterostructures[1, 34, 35]. Inspired by these natural functional adaptive soft tissues the researchers derive the general principle to design and fabricate the high-performance adaptive gel materials.

In this article, we summarize our recent work on high-performance adaptive gel materials with synergistic heterostructures inspired by biological soft tissues, mainly discussing the critical design criteria and fabrication strategies of heterogeneous polymer network architectures within adaptive gel materials. We also discuss the functional adaptive properties of recently reported gel materials, including temperature, wettability, mechanical and shape adaption.

BIOINSPIRED DESIGN OF ADAPTIVE GEL MATERIALS WITH SYNERGISTIC HETEROSTRUCTURES

Biological soft tissues in nature often display effectively adaptive properties far exceeding conventional hydrogel materials[1, 36, 37]. It is due to the dynamic coexistence of synergistic heterostructures, which guarantees the highly adaptive performance in complex environments. Importantly, such heterostructures also can inspire researchers to design and fabricate heterogeneous gel networks with high adaptation to various mechanical and environmental conditions[38]. This section is focused on synergistic heterostructures of biological soft tissues and the bioinspired design strategy of heterogeneous network of gel materials (Fig. 2).

Many biological organisms with synergistic coexistence of heterostructures display the amazing functional adaptation, including adaptive mechanical performance and complex shape changing. For example, many echinoderms are able to rapidly and reversibly alter the stiffness of their connective tissues[39–41]. In the case of sea cucumbers, this dynamic morphing occurs within seconds, producing great surviving advantages. Extensive research suggests that such defense mechanism of sea cucumbers stems from the intimate interactions between their internal heterostructures, *i.e.* rigid collagen fibrils and viscoelastic tissue matrices[42, 43]. In the relaxed state, viscoelastic tissue matrices dominate soft and elastic mechanical properties of sea cucumbers. In contrast, when sea cucumbers meet with their predators, they can achieve a remarkable changing of the matrix stiffness between individual fibrils. In the stiffened state, noncovalent interactions derived from rigid collagen fibrils and tissue matrices can greatly reinforce the mechanical performance of

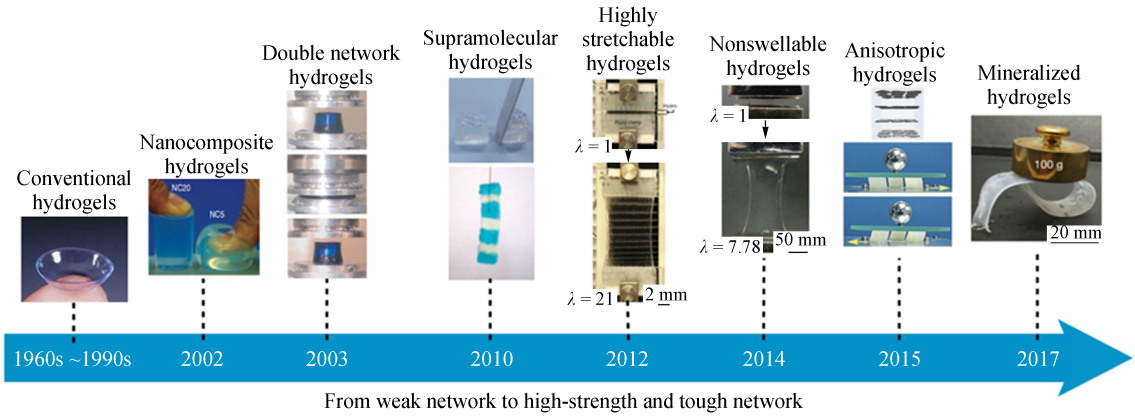


Fig. 1 Timeline presenting major advances in the area of hydrogel research

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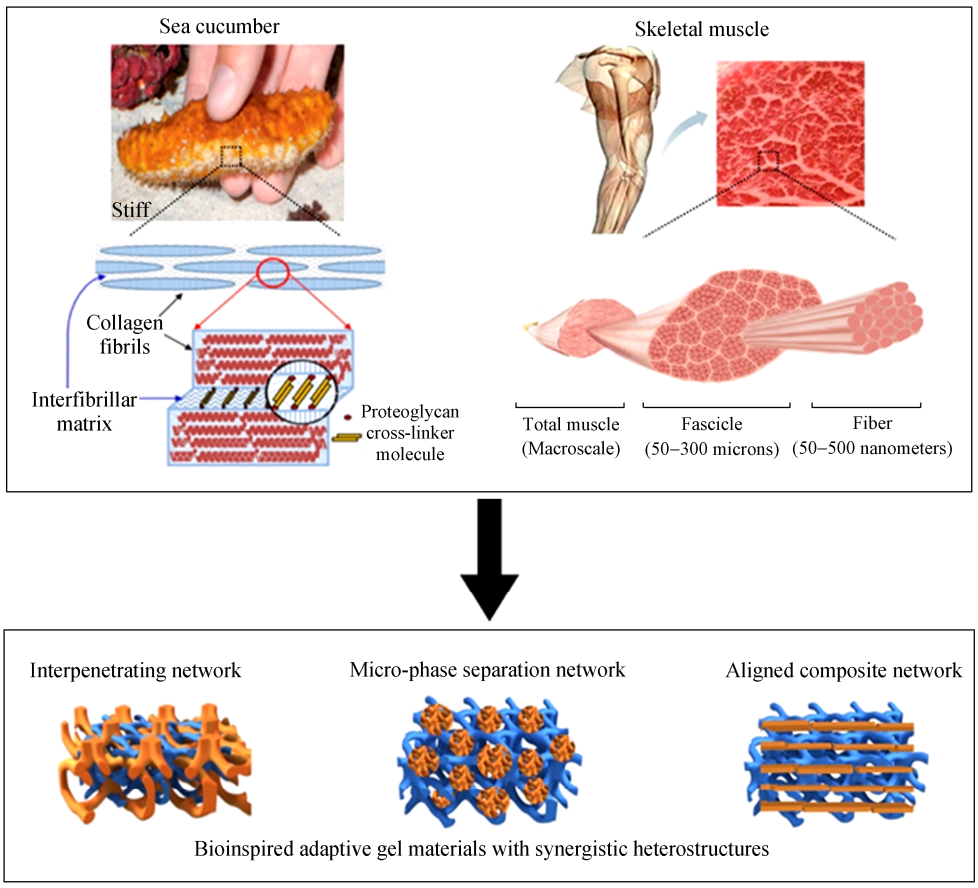


Fig. 2 Schematic illustration of the heterogeneous structures of biological soft tissues, including sea cucumber and skeletal muscles (Such biological heterostructures can provide an inspiration for the design of adaptive gel materials with synergistic heterostructures.)

their inner dermis. Moreover, during this morphing process, these rigid collagen fibrils form the aligned structure within tissue matrices, further enhancing their mechanical strength.

In human bodies, many soft tissues with typical composite heterostructures exhibit highly controllable shape changing and anisotropic mechanical strength, whose functionalities adapt to the complex body movements[44]. The skeletal muscle is a crucial soft tissue in the human body. On the macroscopic scale, skeletal muscle features interpenetrating oleophilic/hydrophilic structures, while on the micro-scale hierarchically ordered composite heterostructures range from micrometers in size to the nanoscale[45–47]. Within the skeletal muscle system, the organized muscle fascicles composed of elastic myofibers with highly aligned structures are closely packed and arranged parallel to each other at the micrometer scale. The aligned myofibers surrounded by extracellular connective tissues, composed of myoblasts, fuse together into multinucleated myotubes. Such unique heterostructures in the skeletal muscle system are essential for anisotropic force generation in a specific direction. In a body movement, the skeletal muscle exhibits high mechanical strength along the fiber alignment direction, which can serve as ideal load-bearing tissues for directional shock absorber in the human body[48]. The specific alignment of skeletal muscle can also allow the myofibers to contract or stretch in synergy during movement, thereby control the complex muscle shape changing. Another obvious example is the articular cartilages with two crucial structural features[49–51]. One is liquid-containing structure with high water content, which enables the low friction coefficient, good lubrication and elasticity for dynamic activities of articular cartilages. The other one is the aligned hierarchical structure mainly composed of collagen and proteoglycan. The articular cartilages contain the hierarchically organized collagenous fibers as scaffolds, which are surrounded by a ground substance consisting of protein, polysaccharides or glycosaminoglycans, primarily in the form of proteoglycan that cements together the hierarchical structure of collagen fibers. As a typical soft tissue with hybrid heterostructures, articular cartilages exhibit high support strengths and the anisotropic energy dissipation, resulting in the capacity for adaptation to complicated usage in external circumstances[52–54].

These desirable biological functions of soft tissues derive from their unique synergistic hybrid structures in many levels of hierarchy, which can provide new insights into the designing and fabricating highly adaptive gel materials with synergistic heterostructures. Currently, the structural optimizing of hydrogels with single-phasic polymer networks greatly enhances the mechanical performance of hydrogels. However, owing to the homogeneous structures that are based on randomly dispersed hydrophilic polymer networks, these strong hydrogels with isotropic and unresponsive mechanical performances have weak adaptability, in contrast to the highly adaptive functionalities of biological soft tissues that contain

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highly synergistic heterostructures. This difference is caused by the lack of controllable factors on conventional hydrogelation strategies which can effectively fabricate the heteronetwork structures of gel materials. To address the intrinsic limitations of conventional homogeneous network, the effective incorporation of heterogeneous network in many scales of hierarchy can serve as a central strategy for designing and fabricating adaptive network architectures. Inspired by the unique heteronetworks of biological soft tissues, researchers have developed several kinds of novel heterogeneous networks as the functional scaffolds of gel materials to generate synergistic interactions, which would lead to the desirable adaptabilities in complex environmental conditions.

FABRICATION AND ADAPTIVE PERFORMANCE OF GEL MATERIALS WITH SYNERGISTIC HETEROSTRUCTURES

Until now, we have proposed various adaptive gel materials with heterogeneous networks, including the interpenetrating heteronetwork, micro-phase separation heteronetwork, and highly ordered nanocomposite heteronetwork. To overcome the inherent limitations of conventional hydrogel materials, the synergistic interaction derived from heteronetworks dominates high adaptabilities of gel materials in complex circumstances.

Adaptive Interpenetrating Heteronetwork Organohydrogels with Wide Working Temperature Windows

In cold climates, many biological organisms can adapt to subzero temperatures and resist the damages to cells from extra-/intracellular ice crystals[55, 56]. This amazing adaptability is based on the internal fatty composition that can protect cell membranes from the damage caused by the growth of ice and maintain the normal organism physiologic function. In biological systems, water and fatty molecules as typical opposing components are of great importance to provide organisms with complementary functionalities (for example, the elasticity and freezing tolerance)[57–59]. However, unlike many biological organisms with low temperature adaptability, artificial hydrogels composed of pure hydrophilic network inevitably freeze and lose elasticity at subzero temperatures. Inspired by such freezing tolerance mechanisms found in nature, we developed adaptive interpenetrating heteronetwork organohydrogels with wide working temperature windows (−78 °C to 80 °C)[60, 61].

To synthesize the interpenetrating heteronetwork organohydrogels, we firstly fabricated a polymer network through thermal polymerization of *N*,*N*-dimethylacrylamide (DMA) in the presence of methylene-bis-acrylamide as a crosslinker. In this case, hydrophilic network can act as a hydrogel matrix. Then organogel precursor solutions containing lauryl methacrylate (LMA) and *n*-butyl methacrylate (BMA) as oleophilic monomers and ethylene glycol dimethacrylate (EGDMA) as crosslinker were introduced into PDMA hydrogel matrix swollen with amphiphilic solvents. Finally, the interpenetrating heteronetwork organohydrogels can be obtained through *in situ* polymerization of oleophilic monomers and crosslinker. The fabrication sequence of the interpenetrating heteronetwork organohydrogels is schematically displayed in Fig. 3(a). In our gel system, the combination of hydrophilic/oleophilic polymers within interpenetrating heteronetworks allows gels to reconfigure their surfaces in response to the adjacent liquid phases. Consequently, such gel materials can switch their surface composition and related features, adapting complex multimedia-based environments. For example, our gel materials are dual superlyophobic when alternately equilibrated in water and oil, and such adaptive surface nature shows high reversibility in response to the changing natures of the surrounding phase. Meanwhile, such opposite solvents and networks play complementary roles on the organohydrogels material's wide working temperature windows. In general, the solvent composition and content determine the mechanical performance of organohydrogel materials to a certain extent. The freezing effect of solvents influences the elasticity of materials. For example, water as a dispersion medium within hydrogels was inevitably frozen at subzero temperatures, leading to elasticity loss of hydrogel network. As shown in Fig. 3(b), the temperature effect on the separate hydrogel components of the interpenetrating heteronetwork gels indicates that the storage modulus (G') of PDMA hydrogels abruptly increases at low temperature, ranging from 0 °C to −20 °C. At this state, the ice-like hydrogels turn into an ice-like solid, which could be easily broken (Fig. 3e). Alternatively, the organogel components swollen with *n*-decane as a dispersion medium can maintain elastic properties at low temperature due to the low freezing point of *n*-decane (−29.7 °C) (Fig. 3d). However, as temperature increases (20–80 °C), the organogels exhibit a significant decrease in G' due to the thermal plasticity of oleophilic polymer network, thereby turning the state from freestanding to non-freestanding (Fig. 3f). In contrast, the interpenetrating heteronetwork organohydrogels can maintain stable elasticity over a wide temperature range. The broadening feature of X-ray diffraction pattern of water frozen inside interpenetrating heteronetworks indicates diminished grain size of ice or discrete crystallization forming in gel materials (Fig. 3c). Thus, the discontinuous ice crystallizing in the polymer network guarantees gels to maintain their elasticity at subzero temperatures, even at temperatures as low as −78 °C (Fig. 3g). At a high temperature range, unlike the organogel with non-freestanding mechanical performance, our gel materials still keep a freestanding state due to the high supporting strength of hydrogel matrix (Fig. 3h). The complementary effect of opposite hetero-networks dominates exceptional wide working temperature windows. Therefore, these adaptive interpenetrating heteronetwork gels can serve as significant and promising smart materials to suit a variety of applications.

Actually, introducing low-freezing organic solvent system into polymer network is an effective strategy to improve the anti-freezing property of gel materials. For example, Wang *et al.* reported that based on synergistic interaction between hydrogel network and H_2O/glycerin binary solvent, their

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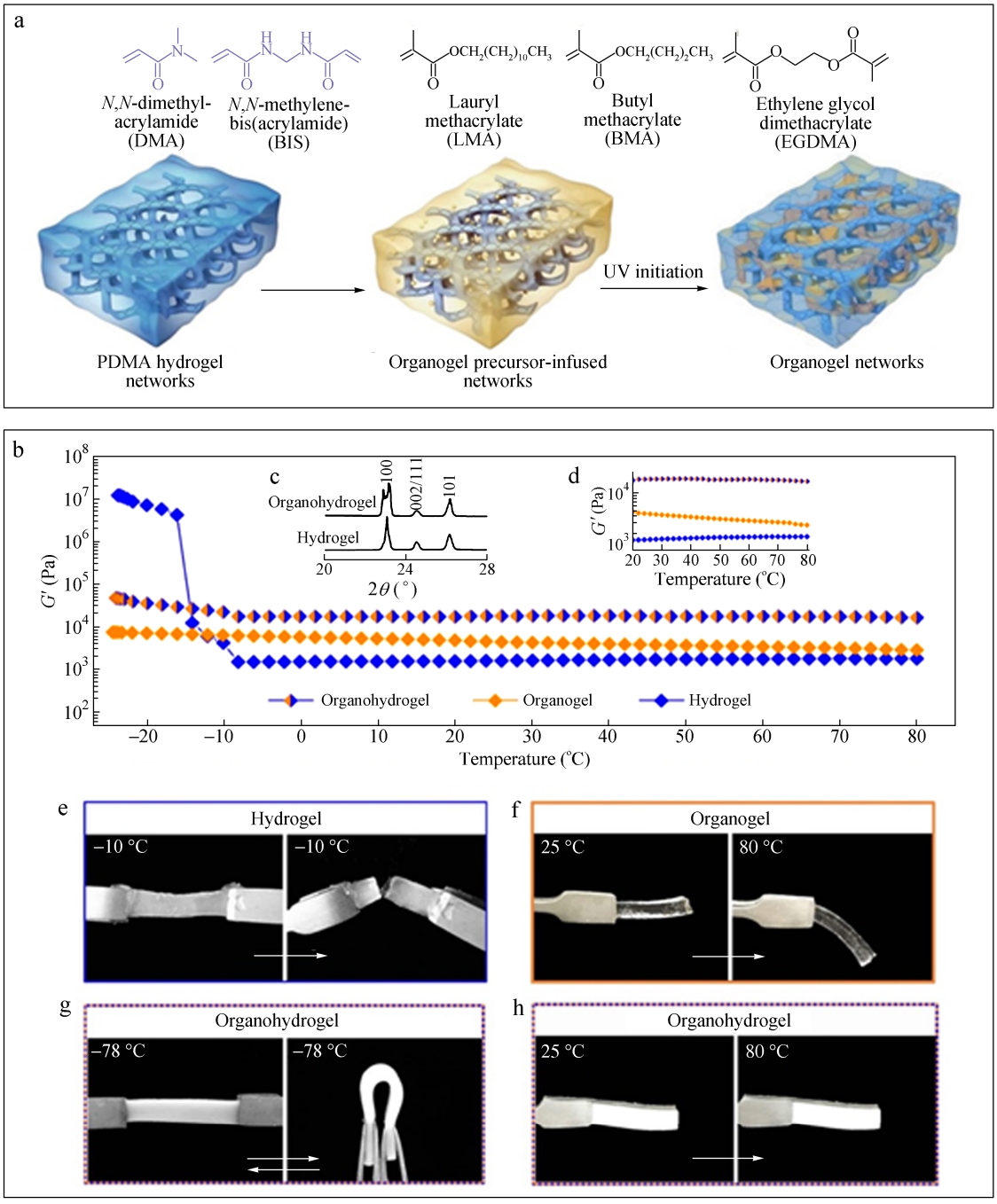


Fig. 3 Adaptive interpenetrating heteronetwork organohydrogels with wide working temperature windows: (a) The monomers and crosslinkers of the hydrogel (blue) and organogel precursors (yellow), and the preparation of the heteronetwork organohydrogels; (b) G' of the hydrogel, organogel and heteronetwork gel on a temperature sweep in the range of –20 °C to 80 °C; (c) X-ray diffraction pattern of water frozen inside hydrogel and heteronetwork gel; (d) The magnified spectra of G' of the gel samples with the changes in temperature; (e) Images showing the ice-like hydrogel that could easily be broken at –10 °C; (f) Images showing the organogel turned into a non-self-standing state when heated to 80 °C; (g, h) Images showing the heteronetwork gel with stable elasticity at both (g) –78 °C and (h) 80 °C (Reproduced with permission from Ref. [60]; Copyright (2017) Nature Publishing Group)

hydrogels exhibit high mechanical performance and anti-freezing property[62]. In our system, *via* incorporation of poly(vinyl alcohol) (PVA) networks and conductive polymers PEDOT:PSS within H_2O/ethylene glycol binary solvent as the anti-freezing dispersion medium, we can realize the stable flexibility and strain-sensitivity of organohydrogel materials at subzero temperatures (Fig. 4a). However, the conventional hydrogels with conductive properties lose not only elasticity but also the ability of conducting electrons at sub-freezing temperatures of the water phase as the surrounding medium. Our anti-freezing conductive organohydrogels can remain stable electrical conductivity at –40 °C (Fig. 4b). The noncovalent interaction of the PVA network provides self-healing capacity for interpenetrating heteronetwork gels

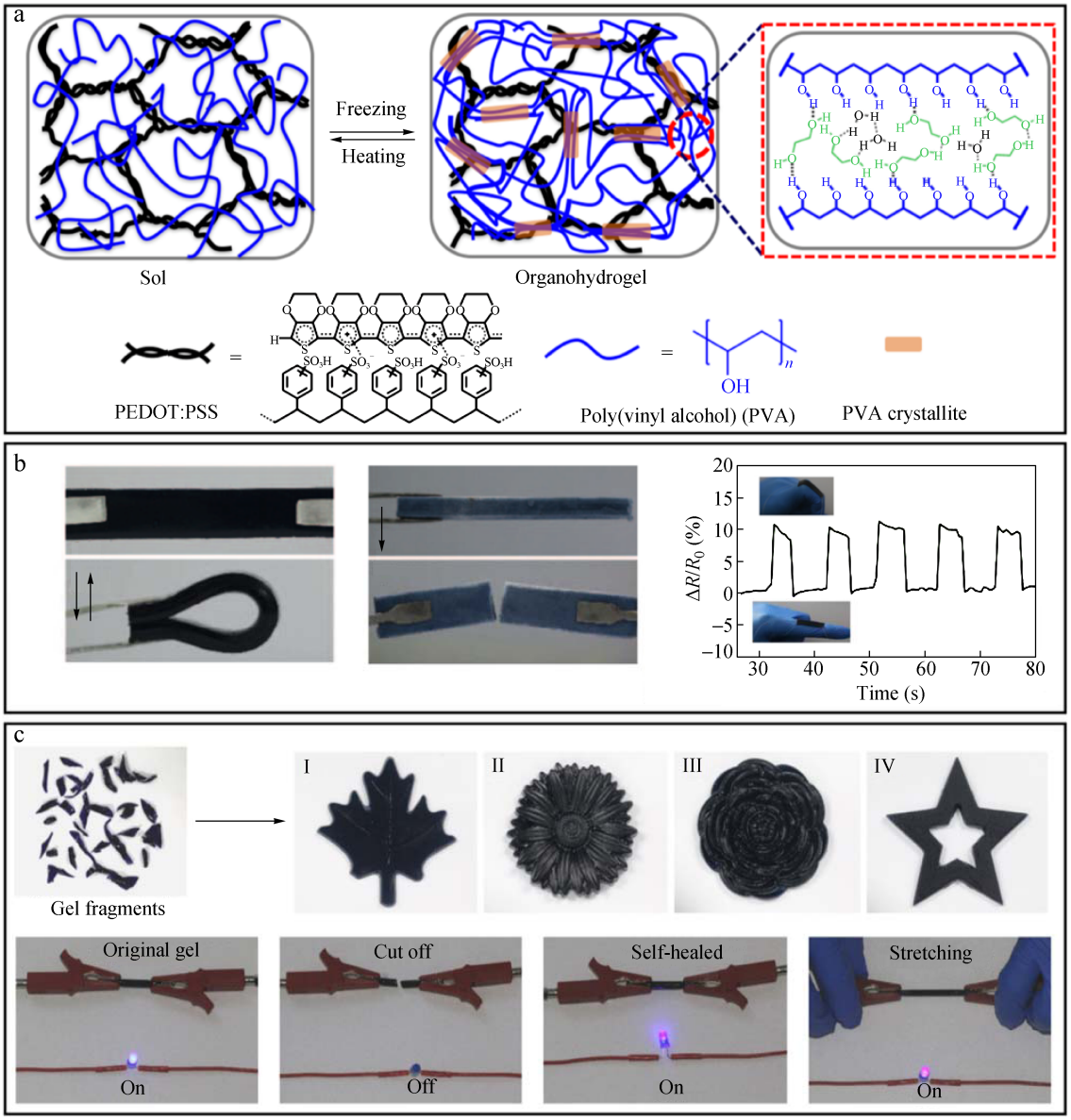


Fig. 4 Adaptive interpenetrating heteronetwork organohydrogels with anti-freezing conductive performance: (a) Schematic illustration of the structural characterization of the anti-freezing conductive organohydrogels with interpenetrating heteronetwork; (b) Images showing their ability of reversible bending at –40 °C; (c) Images showing the remoldability and self-healing properties of the organohydrogel materials (Reproduced with permission from Ref. [61]; Copyright (2017) Wiley-VCH)

(Fig. 4c). Meanwhile, the remoldability of organohydrogel materials can also be obtained due to the thermoplasticity of non-covalent interpenetrating heteronetworks (Fig. 4c). In conclusion, conductive interpenetrating heteronetwork organohydrogels with wide working temperature windows will have promising applications in various fields under extreme cold environment, such as flexible electrode, sensors, energy storage devices, and wear-able devices.

Adaptive Heteronetwork Gels with Functional Surfaces

Adaptive biological interfaces are crucial for various vital activities of biological organisms, such as cell adhesion and proliferation[63–65], nutrient absorption[66], and delivery of genetic information[67]. During these physiological processes, the responsive interfaces, including cell membranes and certain nucleoporin hydrogels, are key prerequisites to the functional adaptation of biological tissues. Thus, constructing functional surfaces by mimicking biological surfaces has become one of the most important subjects for researchers to fabricate adaptive gel-based materials. As a result, a few works about adaptive heteronetwork gels with smart surface wettability have been published by our group.

The *N*-alkylation reaction has been widely used to graft target functional groups onto tertiary amines, thereby being introduced into our work to construct the functional surfaces of hydrogel materials[68, 69]. We firstly prepared hydrogel network, whose surface was covered by the dimethylamino group. Then the as-prepared hydrogel was immersed in an oil phase, *i.e.* dichloromethane. Due to the high-water content, hydrogel network cannot get swollen by the oil phase. Consequently, the surface modification of the *N*-alkylation

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reaction was achieved by immersing the as-prepared hydrogels into an oil phase, in which modifiers were dissolved (Fig. 5a). Figure 5(b) exhibits the stable superhydrophobic surfaces of gel materials due to the existence of the modified superhydrophobic heteronetwork layer. Furthermore, by introducing the photo-responsive molecule (1-(4-iodobutyl)-3,3-dimethylindoline-6-nitrobenzospiropyran) (IBSP) as modifiers, the as-prepared heteronetwork gels can reversibly control their surface wettability in response to ultraviolet (UV) and visible (Vis) light irradiation (Fig. 5c). The underwater oil wettability and underwater oil-adhesion upon this modified hydrogel are also reversibly switched by UV and Vis light illumination, which can be attributed to the photo-responsive ring-opening and ring-closing mechanism of IBSP on heteronetwork gel surfaces.

Adaptive Micro-phase Separation Heteronetwork Organohydrogels with Switchable Mechanics and Controllable Shape Changing

Currently, artificial soft materials like hydrogels mainly depend on homogeneous stimuli-responsive polymer network to adjust their physicochemical properties and mechanical performances. However, most reported stimuli-responsive hydrogel networks depend on the complex molecular design and chemical modification, and these stimuli-responsive hydrogels are mechanically weak[70]. During their responsive process, stimuli-responsive polymer networks easily disintegrate or collapse, causing hydrogels' unstable network structures and mechanical performance[71, 72]. Meanwhile, stimuli-responsive hydrogels with controllable shape changing are mainly based on reversible noncovalent polymer netpoints, such as hydrogen bonding and ionic crosslinking[73–75]. However, such a strategy can typically only realize simple shape shifting, which means that the controllability of shape fixity and recovery from elastic deformation, as in the case of shape memory polymers, is hard to be realized. Also, it is difficult to maintain their shapes and mechanical properties over a long timeframe because of inevitable swelling behaviors under solvent condition. These abovementioned limitations of conventional gel materials tend to restrict their further applications.

To address the inherent limitations of stimuli-responsive homogeneous network, we proposed adaptive micro-phase separation heteronetwork organohydrogels with highly switchable mechanics and controllable shape changing, which

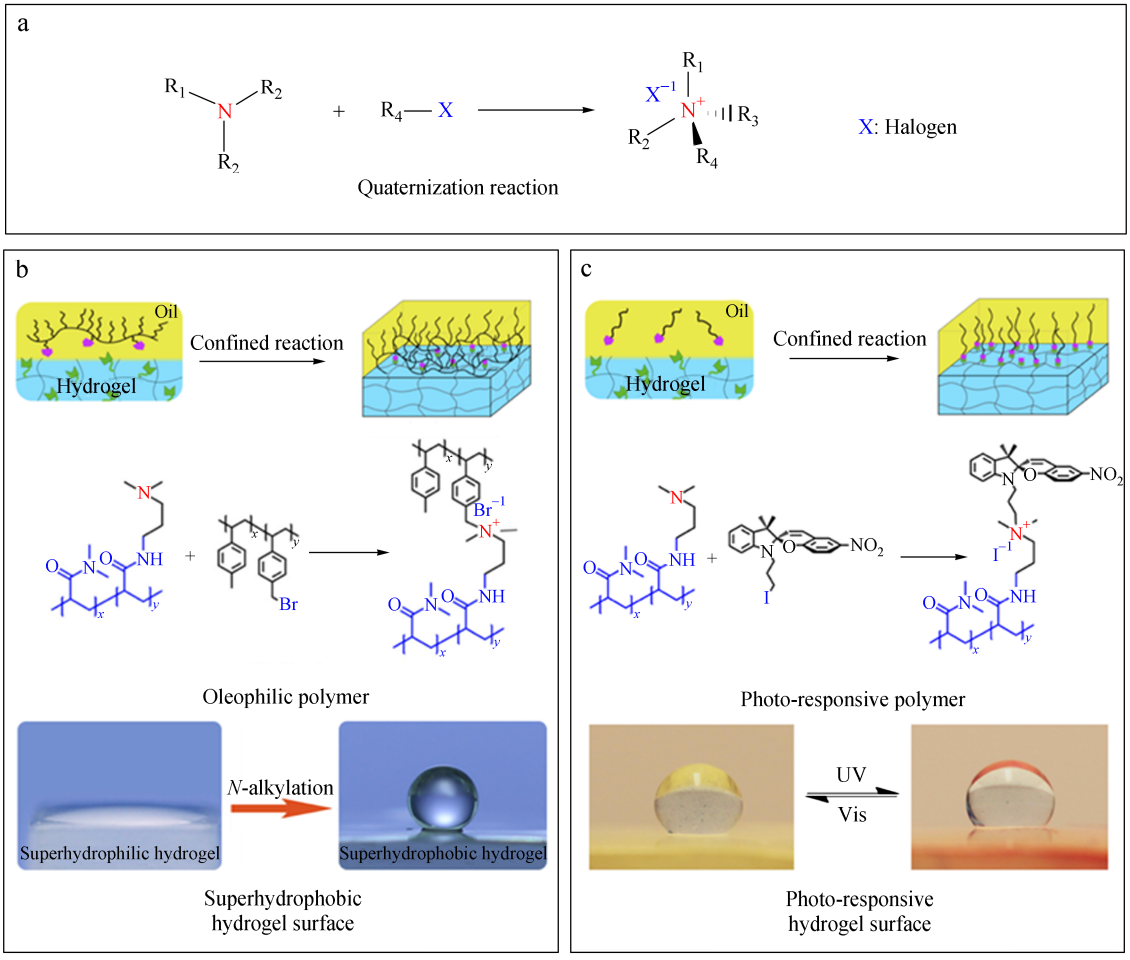


Fig. 5 Adaptive heteronetwork gels with functional surface: (a) Schematic illustration of the quaternization reaction at the heterogeneous interface; (b, c) The functional surface wettability of micro-phase separation heteronetwork gels with images showing the superhydrophobic (b) and photo-responsive (c) surfaces of heteronetwork gels (Reprinted with permission from Refs. [68, 69]; Copyright (2016) Wiley-VCH and Copyright (2017) The Royal Society of Chemistry)

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were synthesized by *in situ* polymerization of an oil and aqueous phase emulsion system[76, 77]. In our work, the oil phase containing molten paraffin, LMA, and EGDMA was emulsified in an aqueous solution of nanoclay and DMA to form a stable oil-in-water emulsion. In emulsion polymerization, gelation occurred in heterophases. The preparation of our organohydrogels is shown schematically in Fig. 6(a). Based on the emulsion polymerization, the hydrophilic polymer network acted as the framework structures, and the oleophilic polymer network act as micro-

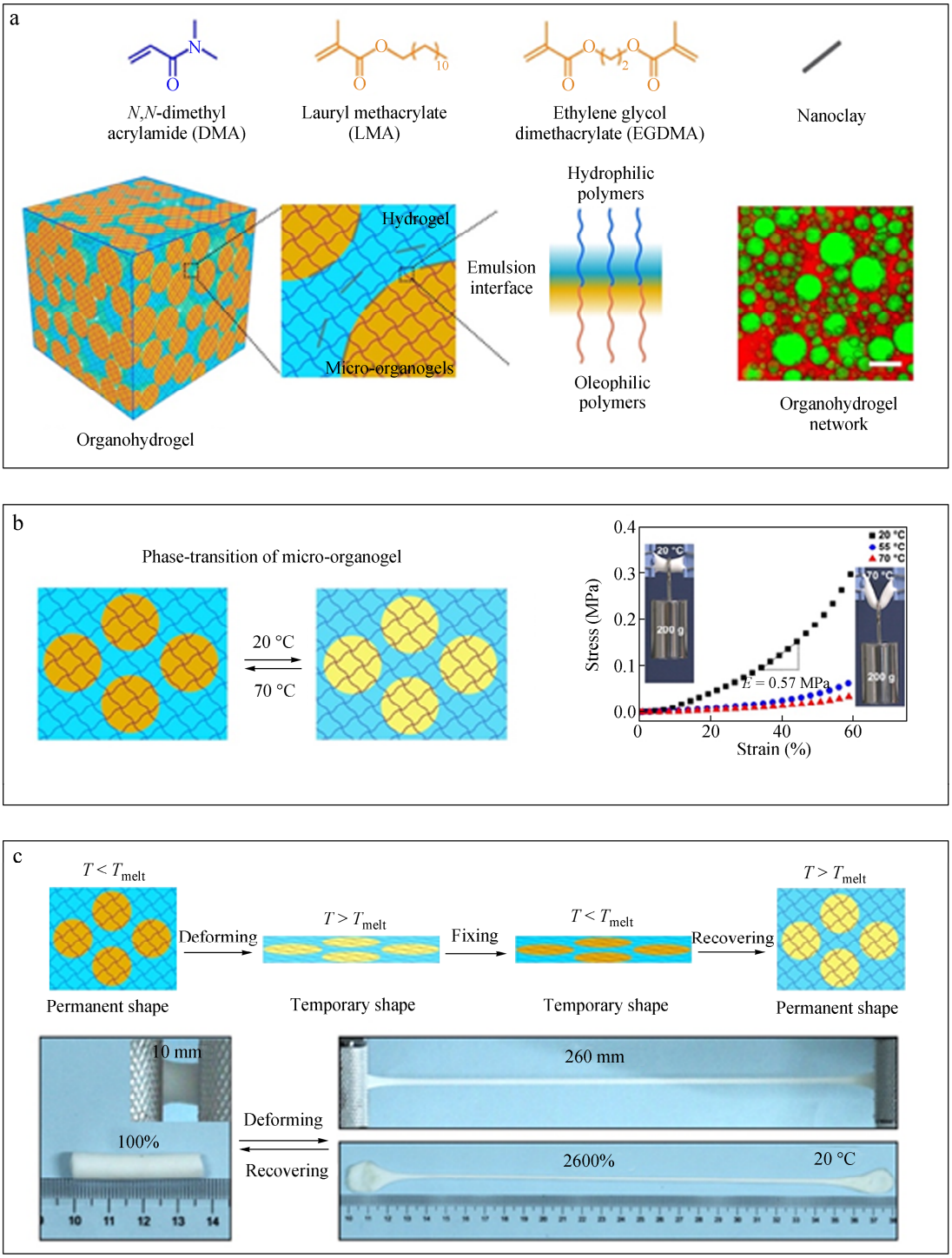


Fig. 6 Adaptive micro-phase separation heteronetwork gels with thermomechanical performance and high-strain shape changing: (a) Schematic illustration of the structural characterization of the micro-phase separation heteronetwork organohydrogels (The scale bar is 20 μm.); (b) The thermomechanical performance of the micro-phase separation heteronetwork organohydrogels and stress-strain curves of the micro-phase separation heteronetwork organohydrogels with applied compression strain at 20, 55, and 70 °C; (c) Shape changing behavior of the micro-phase separation heteronetwork organohydrogels with images showing the high strain capacity of shape changing behaviors in the micro-phase separation heteronetwork organohydrogels) (Reproduced with permission from Ref. [76]; Copyright (2017) Wiley-VCH)

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inclusions. Such micro-phase separation heteronetworks are covalently linked at the emulsion interface. Compared with conventional gels inevitably swollen in the presence of some solvents, our heteronetwork gel materials have the obvious advantage of low-swelling or nonswelling in both oil and water. It is because that the heteronetwork structure of our materials spatially restricts the hydrogel framework and the micro-inclusions with respect to each other. This unique feature of gel materials is important for multimedia applications. Meanwhile, in our case, when the organohydrogel materials are heated above the melting point (T_m) of the paraffin, the molten paraffin serves as a switchable phase within the micro-inclusions (Fig. 6b). Consequently, this phase transition property of the micro-inclusions can trigger the adaptive thermomechanical performance of micro-phase separation heteronetwork organohydrogels. As shown in the inset image of Fig. 6(b), we can observe different deformation of our organohydrogel materials under the same tensile loading at 20 and 70 °C, demonstrating two kinds of applicable mechanical states by applying thermal stimuli: stiff and soft. In compressive tests, the elastic modulus of our materials adaptively decreases with the increasing temperature. The gel sample yields a tangent elastic modulus (E) of 0.57 MPa at 40% strain and 20 °C ($T < T_m$), while the modulus decreases to 0.12 MPa at 55 °C ($T \approx T_m$) and even lowers to 0.053 MPa at 70 °C ($T > T_m$). More importantly, the phase-transition microinclusions and elastic hydrogel framework act synergistically to accomplish highly controllable shape changing. Figure 6(c) illustrates the internal network structure of the micro-phase separation heteronetwork gels during the shape changing process. When the temperature is set above T_m, the liquid state of the paraffin softens the microinclusions. Thus, a certain temporary shape of the gel materials can be easily processed by deformation. When cooling the material below T_m, the temporary shape can be fixed by the frozen paraffin phase. Later, it can fully recover its permanent shape simply by heating the material above T_m. Worth noting is that our micro-phase separation heteronetwork organohydrogels can show high strain property during shape changing process, featuring fully recoverable stretching deformation by up to 2600% (Fig. 6c). Combining the switchable mechanics and controllable shape changing, the micro-phase separation heteronetwork gels will be an ideal candidate for applications requiring high adaptability, such as soft robots, flexible electronics, and biomedical devices.

Recently, based on the research accomplishment mentioned above, we further utilize the synergistic strategy that uses high-internal-phase emulsions (HIPE) to fabricate micro-phase separation heteronetwork organohydrogel materials with high adaptive performance[77]. HIPE as typical biphasic systems contain the total fraction of the continuous/internal phase exceeding 74% by volume. In our case, the high internal oil phase with olephilic stearyl methacrylate (SMA) monomer is emulsified in a PDMA hydrogel precursor solution forming a stable oil-in-water emulsion with internal phase volume fraction up to 0.75. Under UV irradiation, gelation occurs in heterophases (Fig. 7a). Thus, closely packed micro-inclusions within the elastic hydrogel matrix greatly enhance the mechanical performance of the organohydrogel materials. Owing to the switchable phase-transition property of these high internal micro-inclusions, our organohydrogels exhibit excellent switchable mechanics, compared with conventional switchable mechanical hydrogels with unstable single-phasic polymer networks (Fig. 7b). Meanwhile, the self-healing effect of organohydrogels can be obtained due to the noncovalent interaction of biphasic heteronetworks. The continuous hydrogel network with supramolecular nanocomposite structures can serve as the self-healing matrix, and micro-inclusions with strong hydrophobic associations and the crystalline property also have the self-healing ability. Figure 7(c) shows that the healed gel sample easily withstands the stretching and holds a tensile loading of 500 g, illustrating the highly healing efficiency of gel materials. In our system, such switchable mechanics derived from these heterostructures also enable high strain and stiffness as well as shape changing performance of the resulting gel materials (Fig. 7d). Combining the high mechanical strengths, our micro-phase separation heteronetwork organohydrogels can achieve the complicated shape changing control, which is the crucial advantage of our materials compared with the soft hydrogels.

Highly Ordered Heteronetwork Gels with Anisotropic Mechanical Properties

Inspired by the architectural order of cartilages, we designed the long-range ordered heteronetworks within nanocomposite gel materials to enhance the adaptive mechanical properties and functional anisotropy[33, 78]. Firstly, we integrated magnetic field-directed two-dimensional (2D) nanomaterials into polymer network matrixes. When placed in an external magnetic field, these 2D titania nanosheets (TiNSs) become magnetized and act as ordered nano-units within long-range alignment heterostructures, and then nanocomposite gels are prepared by thermal-triggered gelation (Fig. 8a). This producing processing is noncontact, and has no limitation in the size and dimension of nanomaterials. More importantly, our work provides a new possibility for fabricating anisotropic soft materials with highly ordered structures. In the highly ordered gel structures, negatively charged unilamellar TINSs align coaxially in a strong magnetic field, which can keep maximum electrostatic repulsion and thereby induce a quasi-crystalline structural ordering over macroscopic length scales and with uniformly large face-to-face nanosheet separation. This transiently induced structural order is fixed by *in situ* vinyl polymerization. Surprisingly, this gelation procedure does not depend on any additional photocatalyst[79], for unilamellar TiNSs with strong photocatalytic activity can act as photocatalytic crosslinkers that can generate hydroxyl radicals from water to induce radical polymerization. Based on such highly ordered structures, these resultant gel materials exhibit remarkable optical and mechanical anisotropy (Fig. 8b). When bearing the shear forces applied parallel to the embedded nanosheets, these nanocomposite heteronetwork gels are easily deformed, yet resist compressive forces applied orthogonally, thus enabling excellent directional isolation of vibrations (Fig. 8c). This reinforcement of gel materials *via* intrinsic ordered

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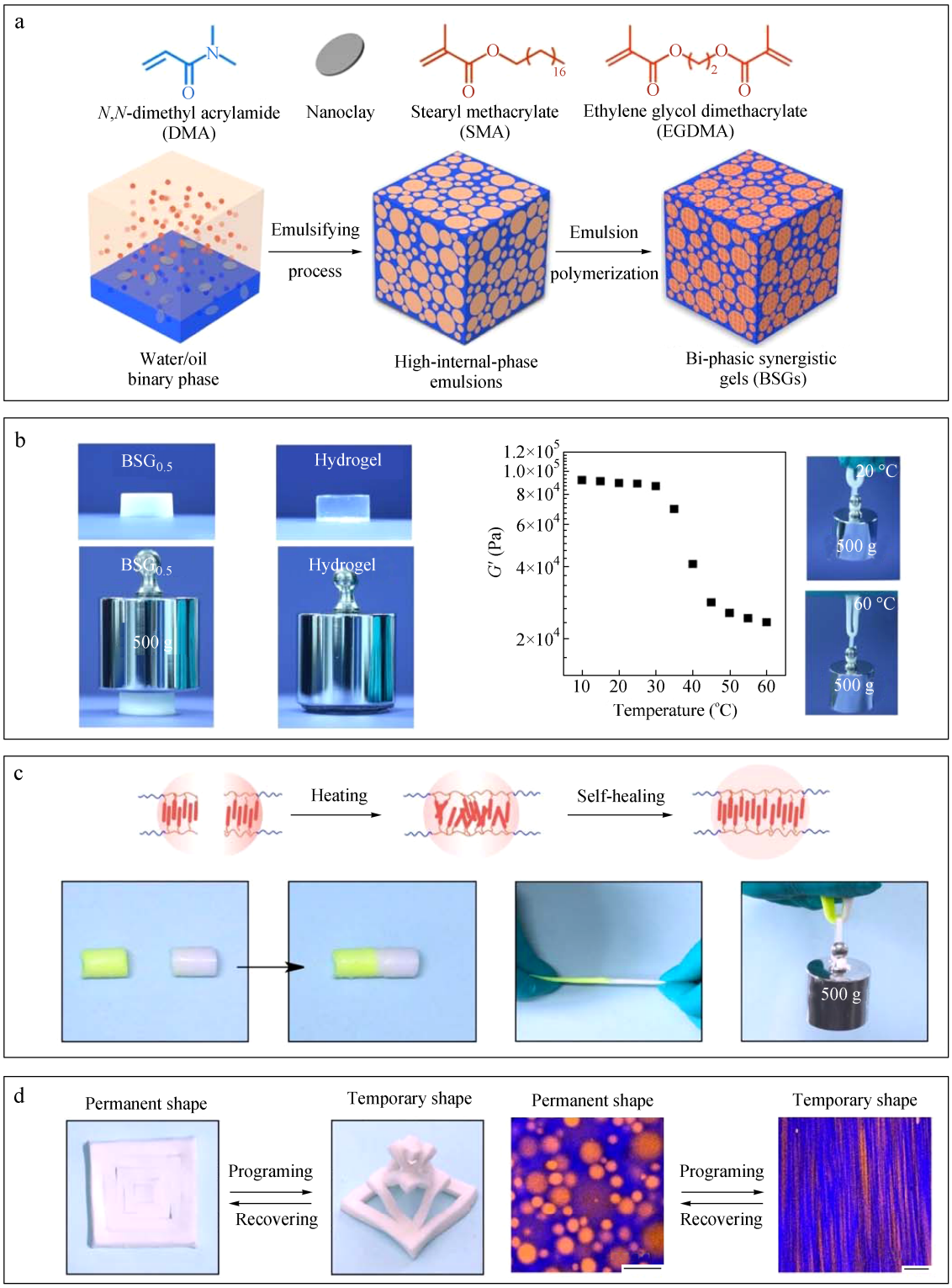


Fig. 7 Adaptive micro-phase separation heteronetwork organohydrogels with switchable mechanics and controllable shape changing: (a) Preparation of the micro-phase separation heteronetwork organohydrogels; (b) The high mechanical strength and switchable mechanics of the micro-phase separation heteronetwork organohydrogels; (c, d) Self-healing effect and controllable shape changing of the micro-phase separation heteronetwork organohydrogels (The scale bar is 10 μm.) (Reproduced with permission from Ref. [77]; Copyright (2017) Wiley-VCH)

nanocomposite structures can be used to create exceptionally strong and elastomeric nanocomposites with properties closely mimicking those of the articular cartilage. Such nanocomposite heteronetwork gel is a new generation of bio-engineering materials with highly adaptive performance. In the follow-up work, Kim *et al.* prepared a highly ordered nanocomposite gel containing thermo-responsive poly(*N*-isopropylacrylicamide) (PNIPAM) network and cofacially

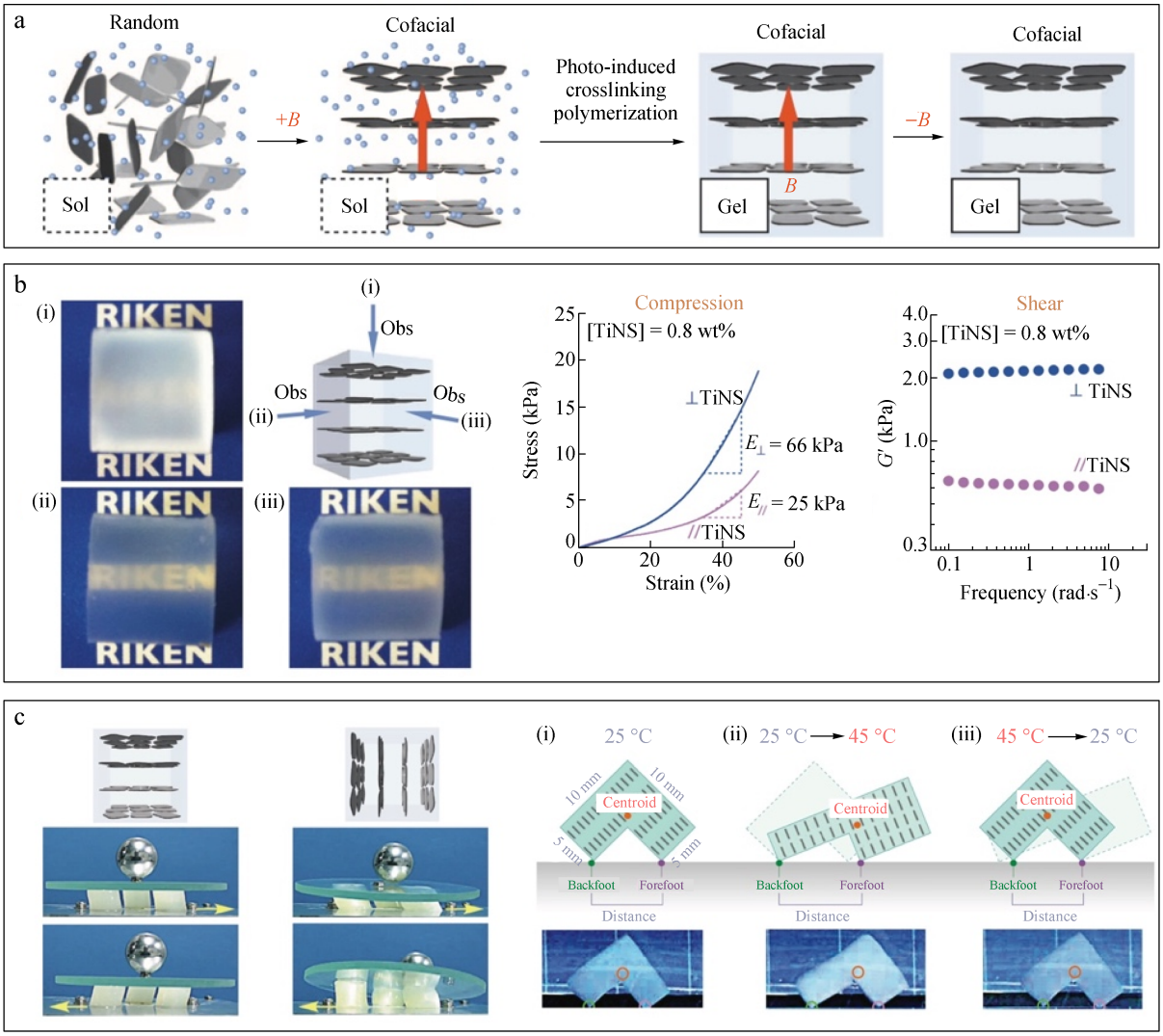


Fig. 8 Highly ordered heteronetwork gels with anisotropic mechanical properties: (a) Schematic illustration of the fabrication process of highly ordered heteronetwork gels; (b) Optical and mechanical anisotropy of gel materials with highly ordered nanocomposite structures; (c) Vibration reducing performance and unidirectional procession of the highly ordered heteronetwork gels (Reproduced with permission from Refs. [33, 78]; Copyright (2015) Nature Publishing Group)

oriented TiNSs. Unlike conventional PNIPAM-based hydrogels that simply shrink and expand in volume and on heating and cooling, the resultant hydrogel with alignment structures have not only opposite but also anisotropic thermal behaviors. This is because thermoresponsive PNIPAM network and anisotropic electrostatic repulsion of cofacially oriented TiNSs act synergistically to control the distance of plane-to-plane nanosheets under thermal stimulus. In heating and cooling process, the distance between the nanosheets rapidly expands and contracts, respectively, resulting in the significant lengthening and shortening of gel materials. Moreover, compared with the simple, omnidirectional active behavior of conventional thermoresponsive gel actuators with the homogenous structures, these L-shaped gel samples with the ordered nanocomposite structures can display directional mechanical motion by applied alternating cycles of heating and cooling (Fig. 8c). Due to these particular features that are derived from the incorporation of such unique ordered structures and thermoresponsive polymer network, these nanocomposite heteronetwork gels can act as ideal soft actuators for diverse applications that are difficult to be achieved by conventional gel actuators.

CONCLUSIONS

In this article, we have mainly summarized the progress of our research works on adaptive gel materials with heterostructures, including interpenetrating heteronetwork, micro-phase separation heteronetwork, and highly ordered nanocomposite heteronetwork. The critical design criteria and the fabrication strategies of heterostructural gel materials have been systemically reviewed. In our gel system, owing to synergistic interactions derived from such heterogeneous structures, gel materials exhibit unique physicochemical properties and desirable functional adaptation that are difficult to be obtained from conventional hydrogels.

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We anticipate that our summary will provide new insights into the design and fabrication of more advanced adaptive gel materials. At present, although our reported heterostructural gel materials possess high adaptation, these materials are not applicable for tissue engineering due to their relatively poor biocompatibility. Moreover, fabrication of adaptive gel materials with both high mechanical strength and strong environment adaptability is still needed. Meanwhile, we suggest a new and important fabrication strategy in adaptive gel materials, that is, the introduction of three-dimensional printing technology to design and fabricate sophisticated macrostructures of gel materials. Finally, heterostructural network can make gel materials more adaptive to complex environments. Development of highly controlled heterostructures will promote progress of adaptive gel materials. Therefore, we believe a new generation of adaptive gel materials with synergistic heterostructures will be presented soon, which will extend further and provide more innovative applications, including their use as soft actuators, intelligent soft sensor devices and advanced engineering materials.

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REFERENCES

1 Zhao, Z.; Fang, R.; Rong, Q.; Liu, M. Bioinspired nanocomposite hydrogels with highly ordered structures. Adv. Mater. 2017, 29(45), DOI: 10.1002/adma.201703045
2 Slaughter, B. V.; Khurshid, S. S.; Fisher, O. Z.; Khademhosseini, A.; Peppas, N. A. Hydrogels in regenerative medicine. Adv. Mater. 2009, 21(32), 3307–3329.
3 Liu, M.; Wang, S.; Jiang, L. Nature-inspired superwettability systems. Nat. Rev. Mater. 2017, 2, 17036.
4 Chen, L.; Yin, Y.; Liu, Y.; Lin, L.; Liu, M. Design and fabrication of functional hydrogels through interfacial engineering. Chinese J. Polym. Sci. 2017, 35(10), 1181–1193.
5 Lee, K. Y.; Mooney, D. J. Hydrogels for tissue engineering. Chem. Rev. 2001, 101(7), 1869–1880.
6 Taylor, D. L.; Panhuis, M. Self-healing hydrogels. Adv. Mater. 2016, 28(41), 9060–9093.
7 Yuk, H.; Lin, S.; Ma, C.; Takaffoli, M.; Fang, N. X.; Zhao, X. Hydraulic hydrogel actuators and robots optically and sonically camouflaged in water. Nat. Commun. 2017, 8, DOI: 10.1038/ncomms14230
8 Lee, B. P.; Konst, S. Novel hydrogel actuator inspired by reversible mussel adhesive protein chemistry. Adv. Mater. 2014, 26(21), 3415–3419.
9 Shin, M. K.; Spinks, G. M.; Shin, S. R.; Kim, S. I.; Kim, S. J. Nanocomposite hydrogel with high toughness for bioactuators. Adv. Mater. 2009, 21(17), 1712–1715.
10 Shin, S. R.; Jung, S. M.; Zalabany, M.; Kim, K.; Zorlutuna, P.; Kim, S. B.; Nikkhah, M.; Khabiry, M.; Azize, M.; Kong, J.; Wan, K. T.; Palacios, T.; Dokmeci, M. R.; Bae, H.; Tang, X.; Khademhosseini, A. Carbon-nanotube-embedded hydrogel sheets for engineering cardiac constructs and bioactuators. ACS Nano 2013, 7(3), 2369–2380.
11 Culver, H. R.; Clegg, J. R.; Peppas, N. A. Analyte-responsive hydrogels: intelligent materials for biosensing and drug delivery. Acc. Chem. Res. 2017, 50(2), 170–178.
12 Xing, J. F.; Zheng, M. L.; Duan, X. M. Two-photon polymerization microfabrication of hydrogels: an advanced 3D printing technology for tissue engineering and drug delivery. Chem. Soc. Rev. 2015, 44, 5031–5039.
13 Wang, P.; Sun, J.; Lou, Z.; Fan, F.; Hu, K.; Sun, Y.; Gu, N. Assembly-induced thermogenesis of gold nanoparticles in the presence of alternating magnetic field for controllable drug release of hydrogel. Adv. Mater. 2016, 28(48), 10801–10808.
14 Liu, J.; Tan, C. S.; Yu, Z.; Lan, Y.; Abell, C.; Scherman, O. A. Biomimetic supramolecular polymer networks exhibiting both toughness and self-recovery. Adv. Mater. 2017, 29(10), DOI: 10.1002/adma.201604951
15 Liu, Z.; Calvert, P. Multilayer hydrogels as muscle-like actuators. Adv. Mater. 2000, 12(4), 288–291.
16 VanBemmelen, J. M. Der hydrogel und das kristallinische hydrat des kupferoxydes. Z. Anorg. Chem. 1894, 5, 466–483.
17 Wichterle, O.; Lím, D. Hydrophilic gels for biological use. Nature 1960, 185, 117–118.
18 Jokl, J.; Kopeček, J.; Lím, D. Mechanism of three-dimensional polymerization of the system methyl methacrylate-glycol dimethacrylate. I. Determination of the structure of the three-dimensional product. J. Polym. Sci. A1 Polym. Chem. 1968, 6(11), 3041–3048.
19 Refojo, M. F.; Yasuda, H. Hydrogels from 2-hydroxyethyl methacrylate and propylene glycol monoacrylate. J. Appl. Polym. Sci. 1965, 9(7), 2425–2435.
20 Hicks, G. P.; Updike, S. J. The preparation and characterization of lyophilized polyacrylamide enzyme gels for chemical analysis. Anal. Chem. 1966, 38(6), 726–730.
21 Freeman, A.; Aharonowitz, Y. Immobilization of microbial cells in crosslinked, prepolymerized, linear polyacrylamide gels: antibiotic production by immobilized Streptomyces clavuligerus cells. Biotechnol. Bioeng. 1981, 23(12), 2747–2759.
22 Otake, K.; Inomata, H.; Konno, M.; Saito, S. Thermal analysis of the volume phase transition with *N*-isopropylacrylamide gels. Macromolecules 1990, 23(1), 283–289.
23 Inomata, H.; Goto, S.; Saito, S. Phase transition of *N*-substituted acrylamide gels. Macromolecules 1990, 23(22), 4887–4888.
24 Dong, L. C.; Qi, Y.; Hoffman, A. S. Controlled release of amylase from a thermal and pH-sensitive, macroporous hydrogel. J. Control. Release 1992, 19(1), 171–177.
25 Zhao, X. Multi-scale multi-mechanism design of tough hydrogels: building dissipation into stretchy networks. Soft Matter 2014, 10, 672–687.
26 Haraguchi, K.; Takehisa, T; Ebato, M. Control of cell cultivation and cell sheet detachment on the surface of polymer/clay nanocomposite hydrogels. Biomacromolecules 2006, 7(11), 3267–3275.
27 Haraguchi, K.; Li, H. J. Control of the coil-to-globule transition and ultrahigh mechanical properties of PNIPA in nanocomposite hydrogels. Angew. Chem. Int. Ed. 2005, 44(40), 6500–6504.
28 Gong, J. P.; Katsuyama, Y.; Kurokawa, T.; Osada, Y. Double-network hydrogels with extremely high mechanical strength. Adv. Mater. 2003, 15(14), 1155–1158.
29 Sun, J. Y.; Zhao, X.; Illeperuma, W. R.; Chaudhuri, O.; Oh, K. H.; Mooney, D. J.; Vlassak, J. J.; Suo, Z. Highly stretchable and tough hydrogels. Nature 2012, 489, 133–136.

30 Rauner, N.; Meuris, M.; Zoric, M.; Tiller, J. C. Enzymatic mineralization generates ultrastiff and tough hydrogels with tunable mechanics. Nature 2017, 543, 407–410.
31 Wang, Q.; Mynar, J. L.; Yoshida, M.; Lee, E.; Lee, M.; Okuro, K.; Kinbara, K.; Aida, T. High-water-content mouldable hydrogels by mixing clay and a dendritic molecular binder. Nature 2010, 463, 339–343.
32 Kamata, H.; Akagi, Y.; Kayasuga-Kariya, Y.; Chung, U. I.; Sakai, T. "Nonswellable" hydrogel without mechanical hysteresis. Science 2014, 343(6173), 873–875.
33 Liu, M.; Ishida, Y.; Ebina, Y.; Sasaki, T.; Hikima, T.; Takata, M.; Aida, T. An anisotropic hydrogel with electrostatic repulsion between cofacially aligned nanosheets. Nature 2015, 517, 68–72.
34 Kim, H. N.; Jiao, A.; Hwang, N. S.; Kim, M. S.; Kang, D. H.; Kim, D. H.; Suh, K. Y. Nanotopography-guided tissue engineering and regenerative medicine. Adv. Drug. Delivery Rev. 2013, 65(4), 536–558.
35 Liu, M.; Jiang, L. Dialectics of nature in materials science: binary cooperative complementary materials. Sci. China Mater. 2016, 59(4), 239–246.
36 Oliva, N.; Conde, J.; Wang, K.; Artzi, N. Designing hydrogels for on-demand therapy. Acc. Chem. Res. 2017, 50(4), 669–679.
37 Dou, X. Q.; Feng, C. L. Amino acids and peptide-based supramolecular hydrogels for three-dimensional cell culture. Adv. Mater. 2017, 29(16), 1604062.
38 Wegst, U. G.; Bai, H.; Saiz, E.; Tomsia, A. P.; Ritchie, R. O. Bioinspired structural materials. Nat. Mater. 2015, 14, 23–36.
39 Motokawa, T. Effects of ionic environment on viscosity of Triton-extracted catch connective tissue of a sea cucumber body wall. Comp. Biochem. Physiol. Part B 1994, 109(4), 613–622.
40 Thurmond, F. A.; Trotter, J. A. Morphology and biomechanics of the microfibrillar network of sea cucumber dermis. J. Exp. Biol. 1996, 199, 1817–1828.
41 Szulgit, G. K.; Shadwick, R. E. Dynamic mechanical characterization of a mutable collagenous tissue: response of sea cucumber dermis to cell lysis and dermal extracts. J. Exp. Biol. 2000, 203(10), 1539–1550.
42 Capadona, J. R.; Shanmuganathan, K.; Tyler, D. J.; Rowan, S. J.; Weder, C. Stimuli-responsive polymer nanocomposites inspired by the sea cucumber dermis. Science 2008, 319(5868), 1370–1374.
43 Mo, J.; Prévost, S. F.; Blowes, L. M.; Egertová, M.; Terrill, N. J.; Wang, W.; Elphick, M. R.; Gupta, H. S. Interfibrillar stiffening of echinoderm mutable collagenous tissue demonstrated at the nanoscale. P. Natl. Acad. Sci. USA 2016, 113(42), E6362–E6371.
44 Johnson, M. A.; Polgar, J.; Weightman, D.; Appleton, D. Data on the distribution of fibre types in thirty-six human muscles: an autopsy study. J. Neurol. Sci. 1973, 18(1), 111–129.
45 Tiidus, P. M., "Skeletal muscle damage and repair", Human Kinetics Press, Champaign, IL USA, 2008, p. 37
46 Wakelam, M. J. The fusion of myoblasts. Biochem. J. 1985, 228, 1–12.
47 Wigmore, P. M.; Dunglison, G. F. The generation of fiber diversity during myogenesis. Int. J. Dev. Biol. 1998, 42(2), 117–125.
48 Jana, S.; Levengood, S. K.; Zhang, M. Anisotropic materials for skeletal-muscle-tissue engineering. Adv. Mater. 2016, 28(48), 10588–10612.
49 Kerin, A. J.; Wisnom, M. R.; Adams, M. A. The compressive strength of articular cartilage. Proc. Inst. Mech. Eng. Part H 1998, 212(4), 273–280.
50 Tepic, S.; Macirowski, T.; Mann, R. W. Mechanical properties of articular cartilage elucidated by osmotic loading and ultrasound. Proc. Natl. Acad. Sci. USA 1983, 80(11), 3331–3333.
51 Fratzl, P.; Weinkamer, R. Nature's hierarchical materials. Prog. Mater. Sci. 2007, 52(8), 1263–1334.
52 Simha, N. K.; Carlson, C. S.; Lewis, J. L. Evaluation of fracture toughness of cartilage by micropenetration. J. Mater. Sci. Mater. Med. 2004, 15(5), 631–639.
53 Ker, R. F. The design of soft collagenous load-bearing tissues. J. Exp. Biol. 1999, 202(23), 3315–3324.
54 Bellucci, G.; Seedhom, B. B. Mechanical behaviour of articular cartilage under tensile cyclic load. Rheumatology 2001, 40(12), 1337–1345.
55 Salt, R. W. Survival of frozen fat body cells in an insect. Nature 1959, 184, 1426–1426.
56 Thomashow, M. F. Plant cold acclimation: freezing tolerance genes and regulatory mechanisms. Annu. Rev. Plant Physiol. Plant Mol. Biol. 1999, 50, 571–599.
57 Moellering, E. R. Muthan, B.; Benning, C. Freezing tolerance in plants requires lipid remodeling at the outer chloroplast membrane. Science 2010, 330(6001), 226–228.
58 Takahashi, D.; Imai, H.; Kawamura, Y.; Uemura, M. Lipid profiles of detergent resistant fractions of the plasma membrane in oat and rye in association with cold acclimation and freezing tolerance. Cryobiology 2016, 72(2), 123–134.
59 Martz, F.; Sutinen, M. L.; Kiviniemi, S.; Palta, J. P. Changes in freezing tolerance, plasma membrane H+-ATPase activity and fatty acid composition in Pinus resinosa needles during cold acclimation and de-acclimatio. Tree Physiol. 2006, 26(6), 783–790.
60 Gao, H.; Zhao, Z.; Cai, Y.; Zhou, J.; Hua, W.; Chen, L.; Wang, L.; Zhang, J.; Han, D.; Liu, M.; Jiang, L. Adaptive and freeze-tolerant heteronetwork organohydrogels with enhanced mechanical stability over a wide temperature range. Nat. Commun. 2017, 8, DOI: 10.1038/ncomms15911
61 Rong, Q.; Lei, W.; Chen, L.; Yin, Y.; Zhou, J.; Liu, M. Anti-freezing, conductive self-healing organohydrogels with stable strain-sensitivity at subzero temperatures. Angew. Chem. Int. Ed. 2017, 129(45), 14347–14351.
62 Shi, S.; Peng, X.; Liu, T.; Chen, Y. N.; He, C.; Wang, H. Facile preparation of hydrogen-bonded supramolecular polyvinyl alcohol-glycerol gels with excellent thermoplasticity and mechanical properties. Polymer 2017, 111(24), 168–176.
63 Shin, J.; Lee, J. S.; Lee, C.; Park, H. J.; Yang, K.; Jin, Y.; Ryu, J. H.; Hong, K. S.; Moon, S. H.; Chung, H. M.; Yang, H. S.; Um, S. H.; Oh, J. W.; Kim, D. I.; Lee, H.; Cho, S. W. Tissue adhesive catechol-modified hyaluronic acid hydrogel for effective, minimally invasive cell therapy. Adv. Funct. Mater. 2015, 25(25), 3814–3824.
64 Liu, Y.; Meng, H.; Konst, S.; Sarmiento, R.; Rajachar, R.; Lee, B. P. Injectable dopamine-modified poly(ethylene glycol) nanocomposite hydrogel with enhanced adhesive property and bioactivity. ACS Appl. Mater. Interfaces 2014, 6(19), 16982–16992.
65 Lee, Y. B.; Shin, Y. M.; Kim, E. M.; Lim, J.; Lee, J. Y.; Shin, H. Facile cell sheet harvest and translocation mediated by a thermally expandable hydrogel with controlled cell adhesion. Adv. Healthc. Mater. 2016, 5(18), 2320–2324.
66 Thornton, D. J.; Sheehan, J. K. From mucins to mucus: toward a more coherent understanding of this essential barrier. Proc. Am. Thorac. Soc. 2004, 1(1), 54–61.
67 Weis, K. The nuclear pore complex: oily spaghetti or gummy

bear? Cell 2007, 130(3), 405–407.
68 Yao, X.; Chen, L.; Ju, J.; Li, C.; Tian, Y.; Jiang, L.; Liu, M. Superhydrophobic diffusion barriers for hydrogels *via* confined interfacial modification. Adv. Mater. 2016, 28(34), 7383–7389.
69 Chen, L.; Yao, X.; Gu, Z.; Zheng, K.; Zhao, C.; Lei, W.; Rong, Q.; Lin, L.; Wang, J.; Jiang, L.; Liu, M. Covalent tethering of photo-responsive superficial layers on hydrogel surfaces for photo-controlled release. Chem. Sci. 2017, 8, 2010–2016.
70 Chen, H.; Yang, F. Y.; Chen, Q.; Zheng, J. A novel design of multi-mechanoresponsive and mechanically strong hydrogels. Adv. Mater. 2017, 29(21), DOI: 10.1002/adma.201606900
71 Bilici, C.; Can, V.; Nçchel, U.; Behl, M.; Lendlein, A.; Okay, O. Melt-processable shape-memory hydrogels with self-healing ability of high mechanical strength. Macromolecules 2016, 49(19), 7442–7449.
72 Luo, R. C.; Wu, J.; Dinh, N. D.; Chen, C. H. Gradient porous elastic hydrogels with shape-memory property and anisotropic responses for programmable locomotion. Adv. Funct. Mater. 2015, 25(47), 7272–7279.
73 Wang, W.; Zhang, Y. Y.; Liu, W. G. Bioinspired fabrication of high strength hydrogels from non-covalent interactions. Prog. Polym. Sci. 2017, 71, 1–25.
74 Dai, X. Y.; Zhang, Y. Y.; Gao, L. N.; Bai, T.; Wang, W.; Cui, Y. L.; Liu, W. G. A mechanically strong, highly stable, thermoplastic, and self-healable supramolecular polymer hydrogel. Adv. Mater. 2015, 27(23), 3566–3571.
75 Lu, C. H.; Guo, W.; Hu, Y.; Qi, X. J.; Willner, I. Multitriggered shape-memory acrylamide-DNA hydrogels. J. Am. Chem. Soc. 2015, 137(50), 15723–15731.
76 Zhao, Z.; Zhang, K.; Liu, Y.; Zhou, J.; Liu, M. Highly stretchable, shape memory organohydrogels using phase-transition microinclusions. Adv. Mater. 2017, 29(33), 1701695.
77 Zhao, Z.; Liu, Y.; Zhang, K.; Zhuo, S.; Fang, R.; Zhang, J.; Jiang, L.; Liu, M. Biphasic synergistic gel materials with switchable mechanics and self-healing capacity. Angew. Chem. Int. Ed. 2017, 129(43), 13649–13654.
78 Kim, Y. S.; Liu, M.; Ishida, Y.; Ebina, Y.; Osada, M.; Sasaki, T.; Hikima, T.; Takata, M.; Aida, T. Thermoresponsive actuation enabled by permittivity switching in an electrostatically anisotropic hydrogel. Nat. Mater. 2015, 14, 1002–1007.
79 Liu, M.; Ishida, Y.; Ebina, Y.; Sasaki, T.; Aida, T. Photolatently modulable hydrogels using unilamellar titania nanosheets as photocatalytic crosslinkers. Nat. Commun. 2013, 4, 2029