

# Self-healing Polymeric Hydrogels: Toward Multifunctional Soft Smart Materials

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**Abstract** The concept of self-healing that involves a built-in ability to heal in response to damage wherever and whenever it occurs in a material, analogous to the healing process in living organisms, has emerged a couple of decades ago. Driven primarily by the demands for life-like materials and soft smart materials, therefore, the development of self-healing polymeric hydrogels has continually attracted the attention of the scientific community. Here, this review is intended to give an in-depth overview of the state-of-the-art advances in the field of self-healing polymeric hydrogels. Specifically, recently emerging trends in self-healing polymeric hydrogels are summarized, and notably, recommendations to endow these hydrogels with fascinating multi-functionalities including luminescence, conductivity/magnetism and shape memory *etc.* are presented. To close, the current challenges and future opportunities in this field are also discussed.

**Keywords** Polymeric hydrogels; Self-healing; Multi-functionalities; Smart materials

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## 1. INTRODUCTION

Soft materials are now of great importance in supporting the development of modern society in the same way as hard materials such as metals, concrete, glass, semiconductors, or ceramics. Hydrogels, as a class of representative soft materials which are intermediate state between solid polymers and polymer solutions, are being vigorously exploited.<sup>[1]</sup> The first synthetic hydrogel came into light with fabrication of a copolymer of 2-hydroxyethyl methacrylate and ethylene

dimethacrylate, by Wichterle and Lim in 1954.<sup>[2]</sup> The soft contact lenses were representative of the first hydrogel product constructed by Wichterle in 1961, this breakthrough achievement reflected the clinical application value of polymeric hydrogels and remains one of the most important applications of hydrogels today.<sup>[3]</sup> These materials are polymeric materials characterized by three-dimensional crosslinked networks, the hydrophilic structures of them render their ability to entrap substantial amount of water within the matrix, and could significantly facilitate substance exchange with surrounding aqueous environment.<sup>[4]</sup> In addition, the tissue-like soft and wet nature they possess endows the hydrogels with peculiar biomimicking functions compared to other materials.<sup>[5]</sup> For example, the hydrogels are able to induce volume phase transitions in response to thermal variation as exhibited by sea cucumbers, perform shape memory behaviors similar to living organisms, as well as self-assemble into core-shell hollow structures akin to coconuts. Therefore, with further research, the hydrogels have been progressively developing into smart materials with various functions. More importantly, the tunability of their structural, mechanical, and rheological properties also makes the hydrogels suitable for various applications, including cancer treatment, wound healing, drug and cell delivery, actuators, tissue regeneration and bio-electronics.<sup>[6]</sup>

Although the polymeric hydrogels have received noticeable attention in the area of materials science, their desirable properties are susceptible to stress-induced formation

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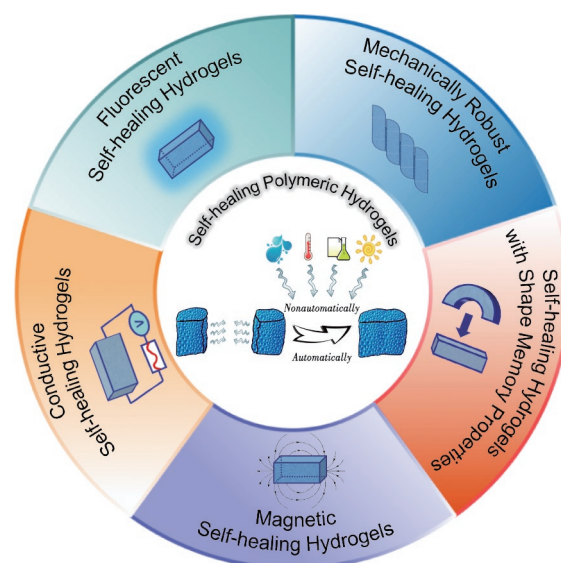
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of cracks. The propagation of these cracks may further impact the integrity of network structures, leading to the deterioration or even loss of functionality and mechanical properties, thereby imposing restrictions on shelf-life and practicability for hydrogels. To prolong their service life span, the capability of recovering functionalities and structures after continual damages, that is, self-repairing or self-healing, has been introduced into the construction of polymeric hydrogels and become the central topic of scientific interests and technological significance.<sup>[7,8]</sup> For example, the ability that a “smart” hydrogel inspired by blue mussel’s secretions can automatically repair damage and regain its associated mechanical properties at low pH, exactly represents self-healing.<sup>[9]</sup>

There have been demonstrated that (i) the coexistence of a “mobile phase” in or around crack areas and (ii) re-bonding of cleaved bonds after mechanical damage are particularly critical for self-healing.<sup>[8]</sup> In the previous work, the presence of free volume was considered as the critical factor to achieve desirable mobility of polymer chains.<sup>[10]</sup> While for hydrogels, their good flow ability facilitates the generation of a “mobile phase” around cracks to fill and bridge the damaged zone for self-healing themselves, ascribable to the solvent contained in hydrogel networks.<sup>[7]</sup> It is therefore that hydrogels have unique advantages over rigid polymers in achieving self-healing performance. For self-healing properties, the dynamic and reversible bonds (crosslinks/reactions) are commonly incorporated directly into the polymeric architectures to realize the recombination of cleaved bonds.<sup>[8]</sup> Remarkably, notable attributes of self-healing hydrogels include the extended lifespan, enhanced durability and intrinsic self-repair affinity, which have been adequately embodied in varying fields, such as soft robotics, tissue engineering and medical devices.<sup>[11]</sup>

Until now, significant progresses have been made in developing self-healing polymeric hydrogels (SPHs), however, the lack of multi-functionalities and mechanical strength/toughness exhibited by SPHs makes this kind of materials still analogous to the conventional hydrogels in terms of properties, therefore, imposing restrictions on the scope of applications in which multiple functionalities are required simultaneously.<sup>[11–13]</sup> Recently there are several excellent reviews on the topic of self-healing hydrogels in terms of healing mechanisms and applications,<sup>[6,7,11]</sup> while those functionalities, especially the luminescent, conductive, magnetic and shape memory properties, which have been verified that those properties can well integrate with other self-healing polymeric materials,<sup>[14–18]</sup> however, were barely reviewed and discussed for self-healing hydrogels combined with these functionalities. In view of this, as shown in Scheme 1, this review mainly aims to introduce state-of-the-art development of self-healing hydrogels with the above unique functionalities and advantageous properties, as well as robust mechanical properties. It starts with a brief presentation of the general strategies to prepare SPHs in Section 2. Subsequently, Section 3 dwells on the evolution of this material toward multifunctional along with tunable mechanical properties. Finally, the review concludes with a perspective on challenges facing the field along with prospects for future development.

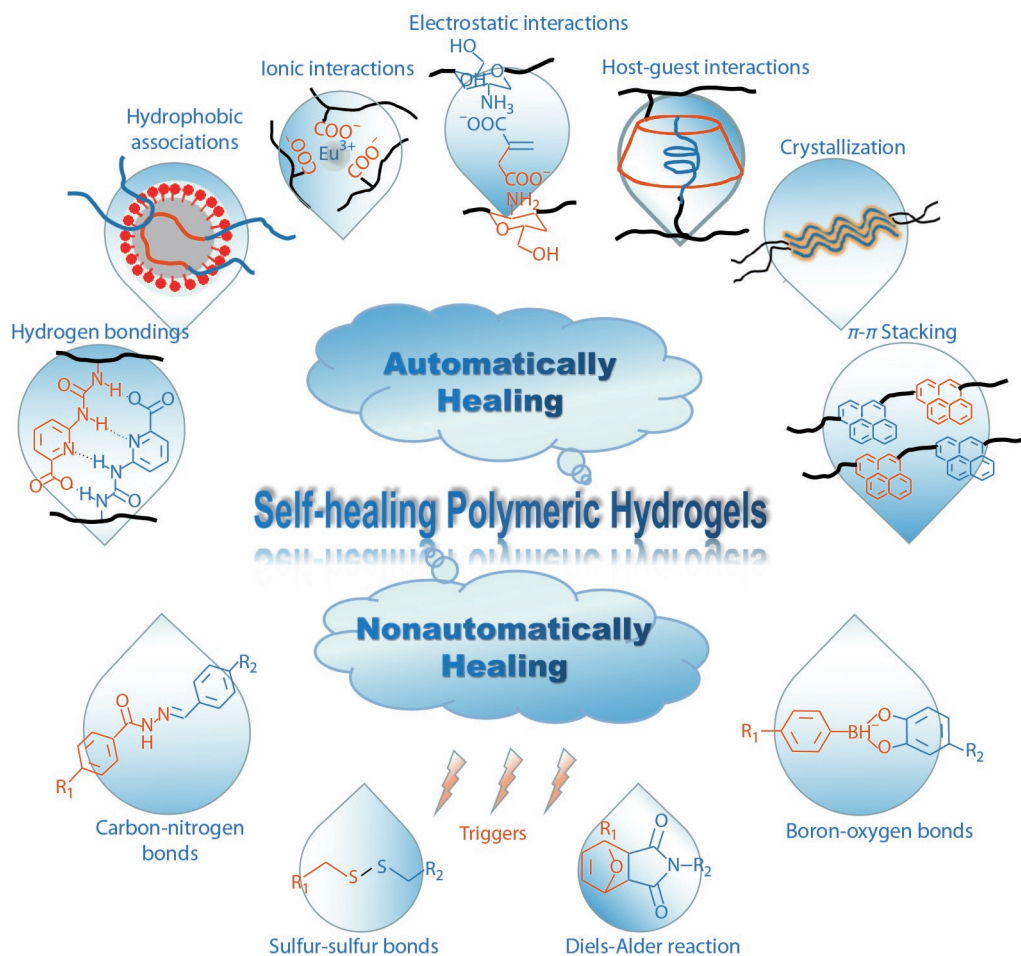


**Scheme 1** The development trend in self-healing polymeric hydrogels.

## 2. APPROACHES TO CONSTRUCTING SELF-HEALING POLYMERIC HYDROGELS

Since the last decades, driven by the technological needs, numerous successful strategies to restore mechanically damaged polymeric hydrogels have been explored.<sup>[2,6–11]</sup> Depending on the additional external energy or trigger (e.g., heat, light, pH or catalyst) whether or not they need to rehabilitate their original structures and properties, the self-healing hydrogels can be mainly classified into nonautomatically and automatically self-healable ones.<sup>[19]</sup> Correspondingly, notable approaches of attaining self-healing polymeric hydrogels consist of dynamic covalent reactions (chemical crosslinking) and noncovalent reactions (physical crosslinking).<sup>[20]</sup>

High bonding strength specific to reversible covalent bonds is the main driving factor for developing chemical self-healing hydrogels, that is, nonautonomous self-healing hydrogels, the application of which can enhance the mechanical toughness of hydrogels.<sup>[8]</sup> As depicted in Fig. 1, concretely, the chemical self-healing hydrogels repair damages by the dynamic formation of covalent bonds, including carbon-nitrogen bonds (imine, acylhydrazone),<sup>[21,22]</sup> sulfur-sulfur bonds (disulfide),<sup>[23]</sup> boron-oxygen bonds (phenylboronate ester)<sup>[24,25]</sup> and Diels-Alder (cycloaddition reversible reaction).<sup>[26]</sup> In general, the dissociation and association of covalent bonds require the applications of an external stimulus or polymerization conditions. While physical crosslinking is primarily realized by dynamic noncovalent interactions such as hydrophobic associations,<sup>[27]</sup> electrostatic interactions<sup>[28]</sup> and supramolecular interactions (e.g. hydrogen bonding,<sup>[29]</sup>  $\pi$ - $\pi$  stacking,<sup>[30]</sup> crystallization,<sup>[31]</sup> host-guest interactions,<sup>[32]</sup> and ionic interactions (metal-coordination)<sup>[33]</sup>), they can be either separately utilized, or in combination. Remarkably, the latter interaction is characterized by reversibility, speed and sensitivity, which makes supramolecular chemistry particularly attractive when it comes to constructing physical self-



**Fig. 1** General strategies used to synthesize self-healing polymeric hydrogels.

healing hydrogels, namely, autonomous self-healing hydrogels.<sup>[8]</sup> In contrast to the self-healing hydrogels fabricated by covalent bonds, these networks within autonomous self-healing hydrogels can be formed reversibly and remodeled rapidly without any external factors. In terms of the design and construction of self-healing hydrogels, the technology innovation of both approaches supplies more diversity and a wider spectrum of properties for soft smart materials.

### 3. TRENDS IN SELF-HEALING POLYMERIC HYDROGELS

#### 3.1 Multi-functional Self-healing Polymeric Hydrogels

We have witnessed that soft smart materials have been becoming a rising star in the area of materials science in the past decade, and especially, those hydrogels with the property of stimulus-response further boosted the research wave of self-healing hydrogels.<sup>[11,21]</sup> By virtue of the capability that the distinctively designed smart hydrogels with self-healing properties respond to certain external stimuli, exhibiting that these materials have great potentiality in a lot of application fields where the specific environmental conditions are inevitable. Apparently, designing stimuli-responsive self-healing hydrogels is liable to endow the same system with functionality beyond self-healing function.<sup>[11,23,24,26]</sup> Accordingly, there is an

increasing interest to develop a next generation of functional hydrogels that allows the self-healing behavior with fast functionality recovery upon damage. And then, the multiple functionalities possessed by SPHs include luminescence, electronic/magnetic and shape memory, will be discussed in detail.

##### 3.1.1 Self-healing polymeric hydrogels with luminescence properties

Luminescent hydrogels hold tremendous potential in many areas particularly ranging from fluorescent sensors, probes, photocatalysts, bioimaging agents to light-emitting devices, as a result of their unique tunable luminous features in absorption (chromogenic) or in emission (fluorochromic) in response to external stimulus.<sup>[34]</sup> Furthermore, it is worth noting that luminescent self-healing hydrogels, a novel functional SPH that combines the merits of tailor-made luminescence emission and self-healing properties, have been more eye-catching recently.<sup>[23,35–46]</sup> Owing to the fact that the molecular structures or assembled states of fluorophores/chromophores will be alternately affected by the loss of mechanical strength and stability of luminescent hydrogels, for example, the fluorescent hydrogels based on spiropyran are vulnerable to luminescence quenching caused by the weak mechanical performance.<sup>[42]</sup> Therefore, it is highly expected to develop the soft materials that could maintain the luminescent-self repaired bifunctio-

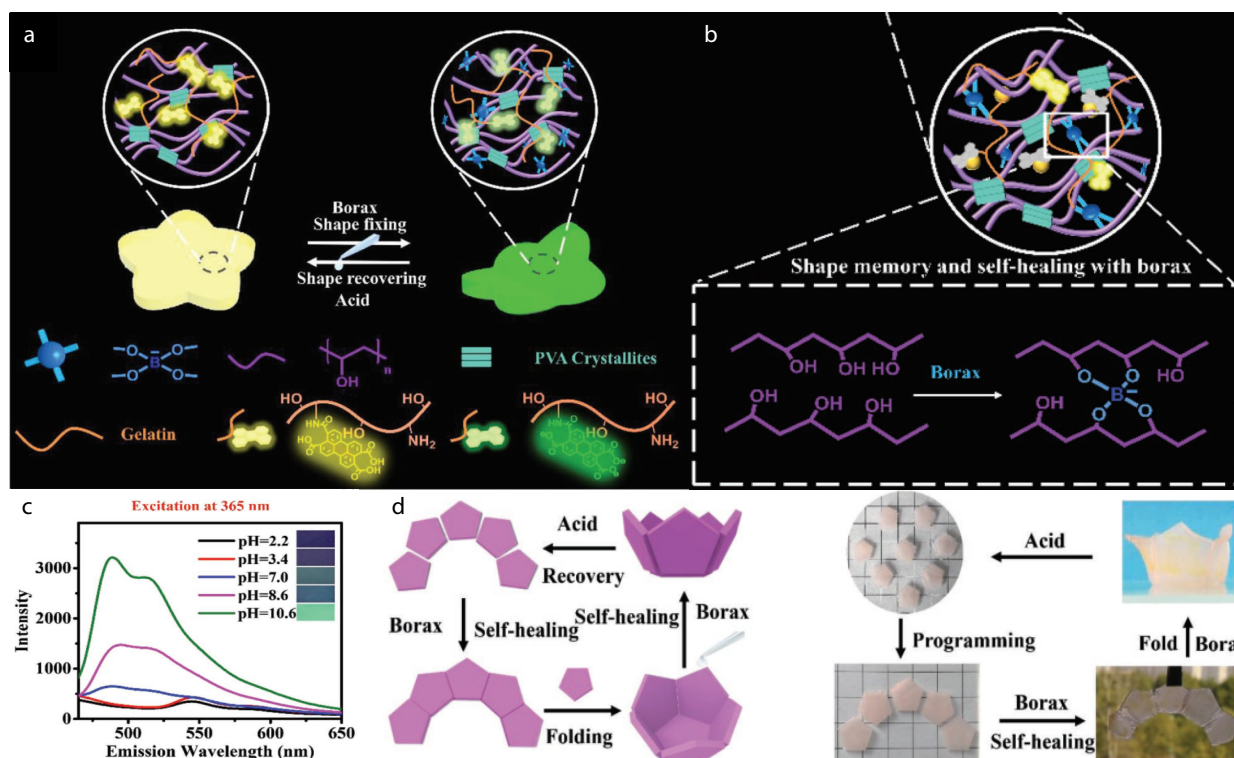
nality after continual damages.

Our group has reported an interesting work that provides an elegant strategy to develop luminescent self-healing hydrogels. We fabricated a typical hydrogel based on perylene-tetracarboxylic-acid-functionalized gelatin/poly(vinyl alcohol) (PVA), which not only exhibits visible emission color change in response to different pH values and “on-off” fluorescent intensity switching behavior induced by  $\text{Fe}^{3+}$  (exposure to 254 and 365 nm), but also possesses robust self-healing and shape memory properties that favor the obtaining of complex 3D hydrogel origami geometries (Fig. 2).<sup>[24]</sup> As for the synergetic effect of these appealing properties, the former originates from the excellent photo-chemical properties of perylene-based fluorophores, which have been employed in many fluorescent hydrogels.<sup>[47,48]</sup> While the latter can be attributed to the highly reversible borate bonds between PVA and borax, a kind of reversibly broken and formed dynamic chemical bond in a mild environment, which helps to sustain fluorescence property after self-healing. The present work is thus able to serve as an information carrier to run commands of information storage, modification and readout, and points out the way for a new potential application for luminescent self-healing hydrogels.

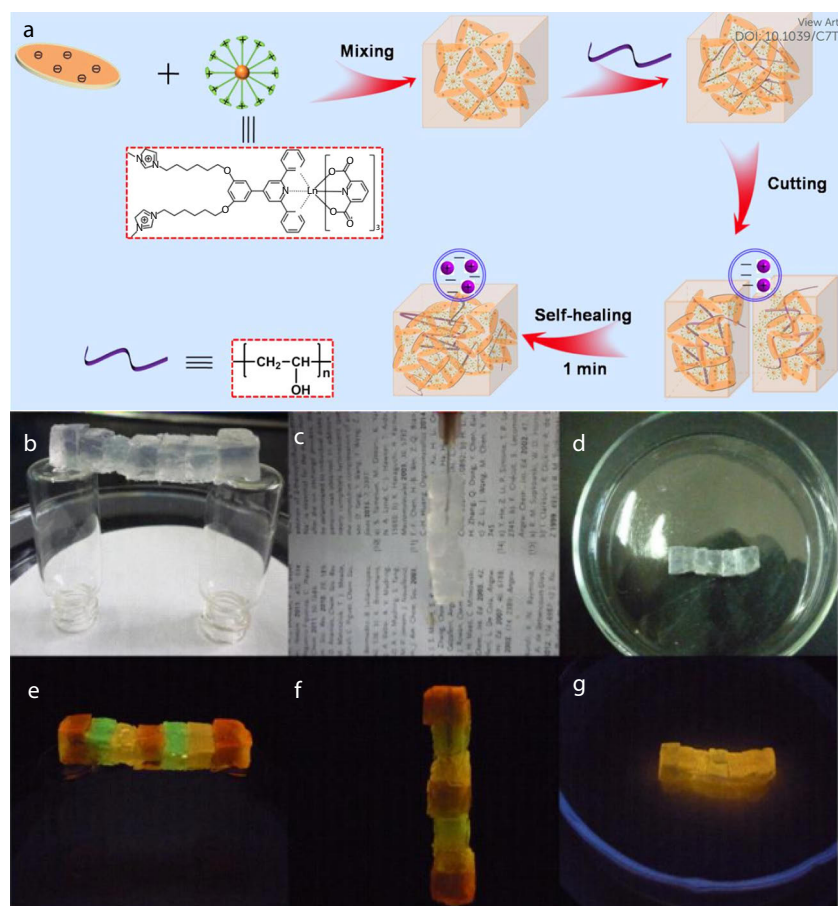
Numerous intriguing strategies also have demonstrated the predominant importance of dynamic chemical bonding for design and construction of luminescent self-healing hydrogels. A hierarchically structured hydrogel composed of hundreds of M13 bacteriophage nanofilaments and a simple

cross-linker, glutaraldehyde (GA) was fabricated, which presents autofluorescence in three channels (358, 498 and 598 nm) due to the reaction between  $\alpha,\beta$ -unsaturated aldehyde polymers in GA and M13 surface proteins, and realizes repetitive self-healing capability at room temperature assisted by the reformation of Schiff's bases formed by M13/calcium interactions.<sup>[35]</sup> After self-healing, hydrogel autofluorescence can still be well preserved after being incubated in PBS or  $\text{CaCl}_2$  for 24 h. Jiang *et al.* integrated with the advantages of dynamic covalent acylhydrazone and disulfide bonds to prepare a self-healing hydrogel with white-light-emitting properties,<sup>[36]</sup> the white light emission of which derives from the incorporation of carbon dots (CDs), Riboflavin and Rhodamine B through a fluorescence resonance energy transfer process. The resulting white light-emitting soft materials based on hydrogels have gained tremendous attractions in the applications of solid-state lighting, message storing and stimuli responsive materials, on account of the inherent green, sustainable and malleable nature of hydrogels.<sup>[37,38]</sup> The self-healing behaviors make this kind of distinctive hydrogels own stable emission colors even after healing process that can take place in a wide range of pH (from 5 to 9 except 7). Obviously, the employment of dynamic chemical bonding may provide a feasible path to exploit the fabrication of luminescent self-healing hydrogels.

Another strategy for the development of luminescent self-healing hydrogels is to make good use of dynamic noncovalent interactions. As shown in Fig. 3, Li *et al.* took advantage of



**Fig. 2** (a, b) Illustration showing the mechanisms of fluorescence response, shape memory and for hydrogels. (c) Fluorescence spectra of hydrogels with 5 freezing–thawing cycles, which are treated by various buffered solutions ranging from pH=2.2 to 10.6 (excitation at 365 nm). Inset shows images of the corresponding hydrogel samples taken under a 365 nm UV light. (d) Six pieces of regular pentagon-shaped hydrogel sheets were brought together and self-healed in the presence of borax solution to form a freestanding 3D hydrogel bowl (Reprinted with permission from Ref. [24]; Copyright (2019) WILEY-VCH).



**Fig. 3** (a) Scheme illustration of the preparation and self-healing process of luminescent hydrogels. (b, c) Self-healing pictures under daylight and (e, f) 254 nm UV lamp illumination after adhesion freshly cut surfaces at 25 °C. (d) After 2 h, the luminescent hydrogels under daylight and (g) under 254 nm UV lamp illumination (Reprinted with permission from Ref. [39]; Copyright (2018) The Royal Society of Chemistry).

the dynamic nature of electrostatic interactions between positive-charged luminescent micelles and negatively-charged clay nanosheets, satisfying the demand for constructing color-tunable luminescent hydrogels with outstanding self-healing abilities at room temperature. Further addition of PVA is likewise beneficial to forming a more stable luminescent hydrogel with fast self-healing performances. The bright luminescence with a quantum efficiency up to 47.6 indicates that the healed hydrogel can retain its original fluorescence, despite of very small portion of lanthanide complexes (~0.08%) and very large portion of water (~97%) contained in the final product.<sup>[39]</sup> The host-guest cognition between a  $\beta$ -cyclodextrin host polymer and an  $\alpha$ -bromonaphthalene polymer was successfully incorporated into a supramolecular polymeric hydrogel to realize the self-healing behavior within only about one minute without any additive.<sup>[40]</sup> This intriguing work also afforded the emitting abilities of room-temperature phosphorescence signals to the hydrogel, which permitted the reversible intensity adjustment upon alternative UV@365 nm and UV@254 nm when introducing another azobenzene guest polymer. The advantage of host-guest interactions was also employed to combine with metal coordination interactions for the fabrication of a new supramolecular polymeric hydrogel with excellent self-healing properties

after being destroyed by external forces.<sup>[41]</sup> Except the thermochromic fluorescence responsiveness displayed by this hydrogel, it also presents multiple stimuli responsiveness induced by competitive ligands. While Zheng *et al.* proposed a double network hydrogel with tunable full-color fluorescence upon excitation of a 980 nm laser. The self-healing properties of the hydrogel can be obtained either at room temperature or at the elevated temperature of 95 °C, the former is mainly ascribed to the re-formation of the second poly(*N*-(hydroxyethyl)acrylamide) network, while the latter with heating treatment can drastically improve the healing effect *via* the sol-gel-induced reorganization of the first agar network.<sup>[42]</sup> These compelling results have demonstrated that dynamic noncovalent interactions may serve as an effective method for the preparation of luminescent self-healing hydrogels.

Dynamic chemical bonding and dynamic noncovalent interactions can not only be used individually, but also in combination. There is an interesting work that designed a heterogeneous composite hydrogel (Gel-C) consisting of three different self-healing hydrogels with yellow, green, and orange fluorescent color upon UV@365 nm irradiation (Gel-Y, Gel-G, and Gel-O), respectively. These different colors are provided by aggregation-induced emission luminogens (AIEgens) that

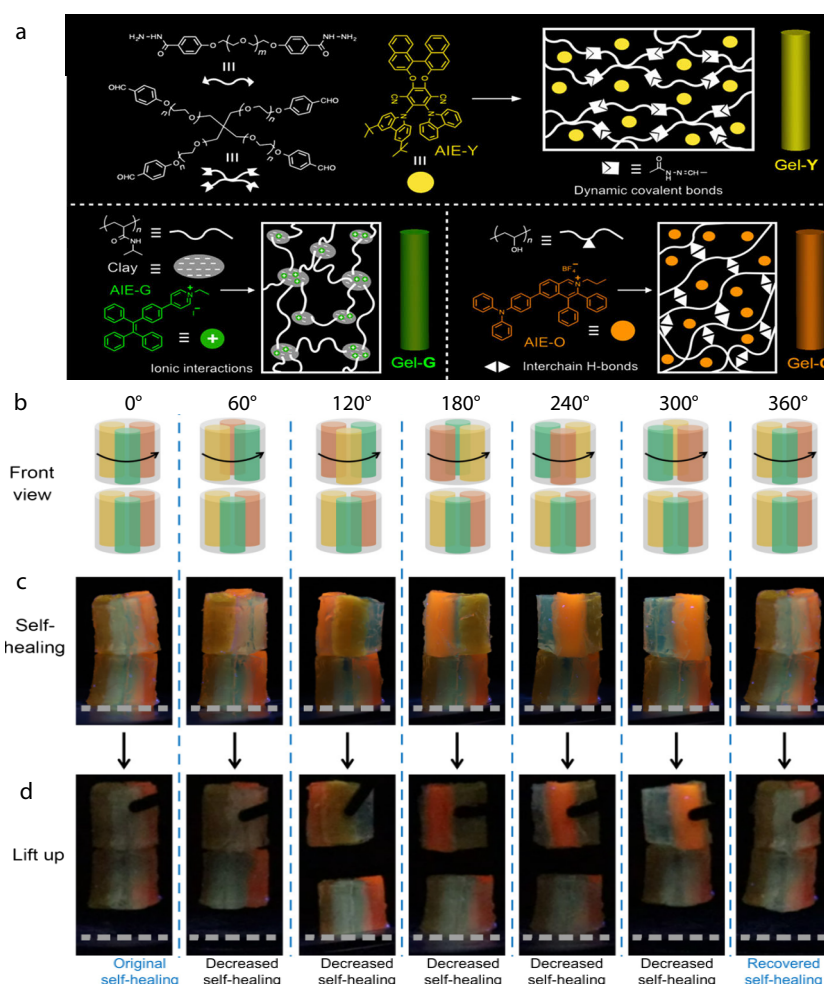
would become highly luminescent when they are aggregated in a concentrated solution or cast into a solid film.<sup>[43,44]</sup> In the case of samples with rotation angles of 0° and 360°, Gel-C exhibits the greatest breaking strain values after healing, whereas the values decrease to different extents in the range of 60°–300° (Fig. 4), implying the positive effect of selective self-healing properties, which can be ascribed to the heterogeneous internal structure and the recognition specificity of each included hydrogel part. The self-healing driven forces of Gel-C are based on hybrid dynamic bonds, which originate from the dynamic acylhydrazone bonds (Gel-Y), the ionic interactions between the polymer and clay surface (Gel-G) as well as the hydrogen bonding (Gel-O), respectively. This system helps to precisely heal different parts, avoiding misalignment repair, attributable to the diverse dynamic interactions between interfaces, namely, the varying self-healing mechanisms.<sup>[45]</sup> Besides, the excellent self-healing abilities as a combined result of the reversible covalent and non-covalent interactions can likewise be observed in the fluorescent chitosan hydrogels.<sup>[46]</sup> The aforementioned work suggests that self-healing properties not only confer upon luminescent SPHS

the extended lifetime but also hold their favorable luminescence performance even suffering from damage.

### 3.1.2 Self-healing polymeric hydrogels with electronic/magnetic properties

Polymeric hydrogels with soft and flexible mechanical properties integrated with electrical conductivity are ideal candidates for various fields such as biomedicine (bioelectronics, electronic skin, etc.) and the electrical field (circuits, sensors, soft robotics, flexible electrodes, etc.).<sup>[49,50]</sup> Conductivity is highly anticipated for hydrogel functionality because it is an indispensable component for most electronic devices to support their normal operation. Hence, the design and development of conductive self-healing hydrogels, for the sake of not only elongating the lifetime of electrical devices, but also retaining the conductivity capability, has generated great interest in research in recent years.<sup>[51–53]</sup>

Our group has developed a nanocomposite hydrogel ionic conductor comprising polyzwitterion-clay, which combines properties of transparency, conductivity, stretchability, biocompatibility, self-healing, and self-adhesive ability that

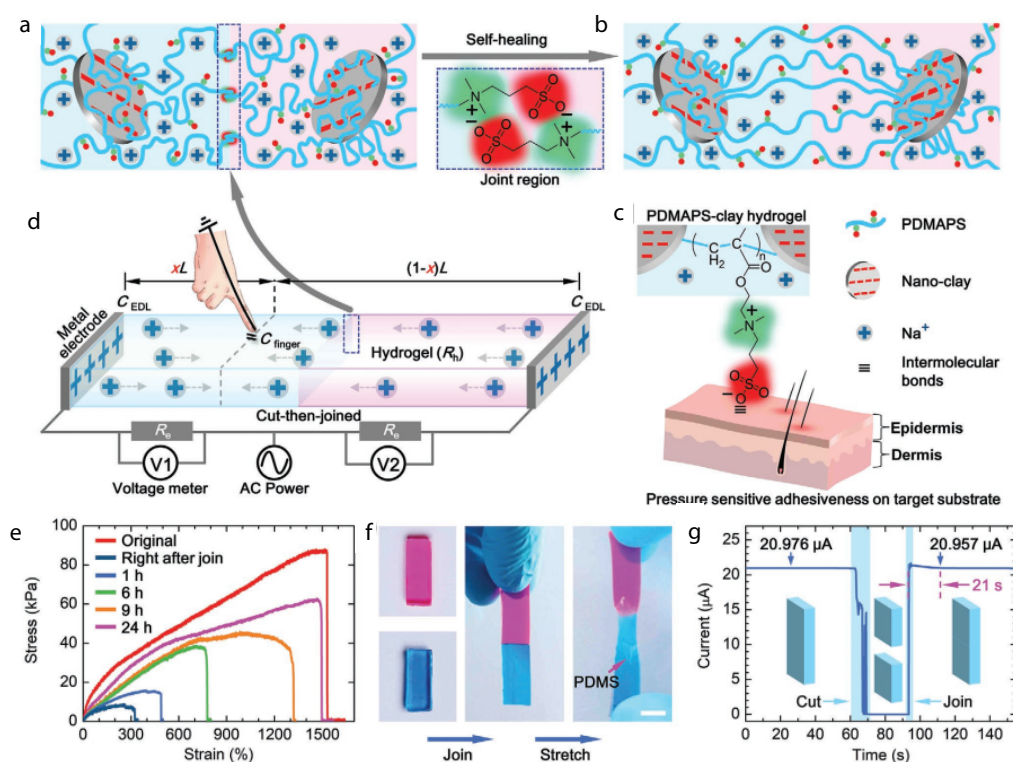


**Fig. 4** (a) Cartoon representations and chemical structures of different hydrogels. (b–d) Cartoon representations, fluorescence images ( $\lambda_{\text{ex}}=365$  nm) from front view, and lift up processes of the self-healed cylindrical hydrogel Gel-C when one broken part was rotated through different angles. Note: the healing time was 50 h (Reprinted with permission from Ref. [45]; Copyright (2020) Chinese Chemical Society).

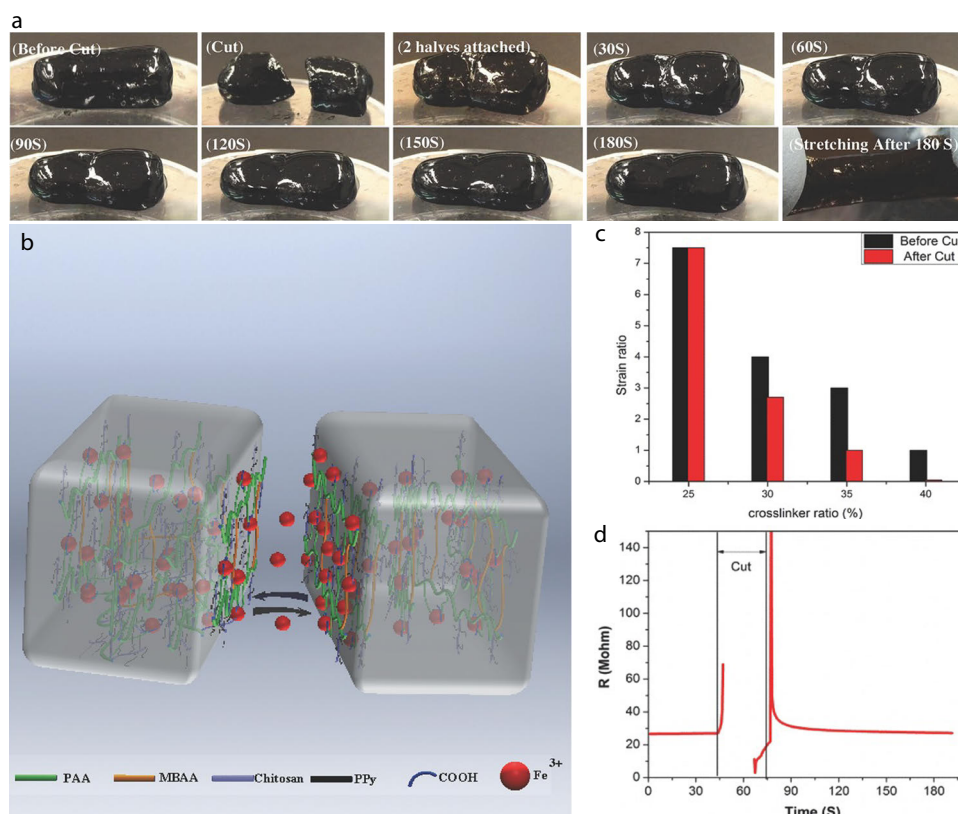
can be used as a human-machine interactive touch pad with pressure-sensitive adhesiveness on target substrates (Fig. 5).<sup>[51]</sup> The presence of polar zwitterion groups and non-covalent crosslinking accounts for the fast self-healing nature owned by this conductive nanocomposite hydrogel within only 21 s, meanwhile, the capability of instantaneous healing is essential for the recovery of electrical conductivity *via* rebuilding ion channels in hydrogels. This heartening work opens up the possibility of using the conductive self-healing hydrogels as flexible human-machine communication interfaces. Another conductive nanostructure of polypyrrole networks together with physically and chemically crosslinked networks offers new applications in strain and pressure sensing devices with bulk conductivity, mechanical and electrical self-healing properties, ultrastretchability, and pressure sensitivity.<sup>[52]</sup> As shown in Fig. 6, the dynamic ionic interactions between carboxylic groups of poly(acrylic acid) (PAAc) and ferric ions result in the intrinsic self-healing of hydrogels, which enables the mechanical recovery and 90% of electrical recovery within 2 min and 30 s, respectively. As a stretchable wireless human motion detector is successfully fabricated, the practical potential of conductive self-healing hydrogels is further revealed by their application in wearable devices. Besides, Wang *et al.* developed a kind of stretchable, conductive and self-healing hydrogel fibers (PNA) for strain sensing, whose conductivity and healing efficiency reach up to  $0.69 \text{ S}\cdot\text{m}^{-1}$  and 85%, respectively, after 10 min healing at  $60^\circ\text{C}$ .

With the elastomeric poly(methylacrylate) (PMA) coatings, the obtained PNA/PMA core-sheath fiber has been demonstrated for monitoring human body motion on account of its splendid strain sensing capability.<sup>[53]</sup> This kind of stretchable conductive self-healing hydrogel fibers is highly promising for next-generation multifunctional smart textiles and wearable electronics.

Remarkably, it is highly anticipated that biomimetic human skin-like materials with preferably self-healing ability may serve as platforms for transducing diverse external stimuli into detectable electronic signals, in order to imitate the flexible and sensory performances of the human skin. Among the diverse bioinspired skin materials, those based on conductive SPHs are of particular interest.<sup>[12,49,52]</sup> For example, Wu *et al.* fabricated a novel bioinspired mineral hydrogel consisting of very small amorphous calcium carbonate (ACC) nanoparticles physically crosslinked by PAAc and alginate chains. It has been demonstrated that this hydrogel could be employed as a recyclable, highly sensitive, mechanically compliant to curved and dynamic surfaces, and autonomously self-healable ionic skin to detect the subtle changes in external pressure, including a gentle finger touch, human motion, and even small water droplets (mimicking raining).<sup>[54]</sup> This outstanding work suggests great potentials for the development of next-generation mechanically adaptable intelligent skin-like devices. These aforementioned results indicate that spontaneous healing of the developed conductive self-healing hy-



**Fig. 5** Position sensing on self-healing and adhesive polyelectrolyte-clay nanocomposite hydrogels. (a, b) Schemes illustrating cut hydrogels healed by electrostatic attraction between polyelectrolytes (a) and rebuilding polyelectrolyte-clay adsorption (b). (c) Schematic illustration of hydrogels adhered to the skin through intermolecular bonds. (d) The architecture of 1D hydrogel touch strip. (e) Stress-strain curves of hydrogel and hydrogels healed for different times. (f) Photos of two freshly cut hydrogel sections joint together and stretched by hands. (g) The current in a hydrogel varied by time, when it was intact, cut, and joined (Reprinted with permission from Ref. [51]; Copyright (2020) WILEY-VCH).



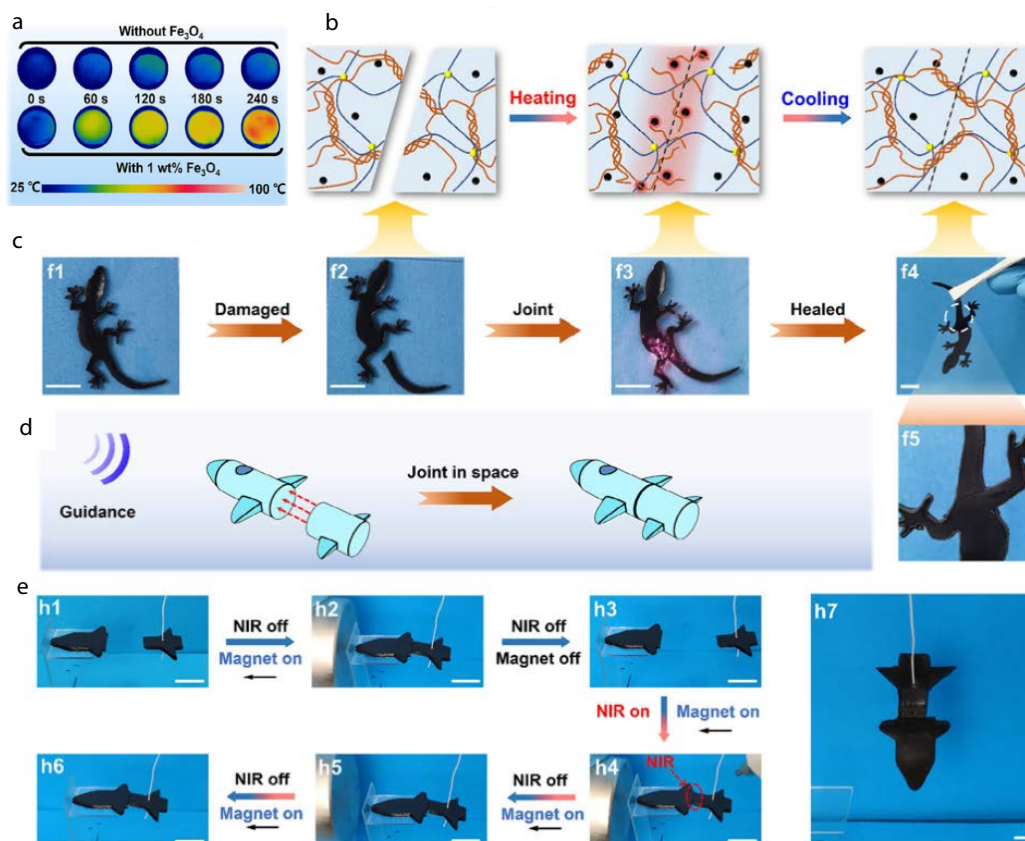
**Fig. 6** Self-healing property of the hydrogel. (a) The hydrogel was cut into two halves and then brought together again; each 30 s, the hydrogel is shown enabling us to track the vestige of cut. (b) Schematic mechanism of healing after the cut. (c) Self-healing recovery efficiency (strain ratio before cut and after healing) (samples were prepared in rod shape with 8 mm diameter and 1 cm length). (d) Capability of electrical recovery after cut, showing 90% of electrical recovery in 30 s. It is seen after 1 min, the electrical recovery efficiency is 96%. Rheology examination of the hydrogel (Reprinted with permission from Ref. [52]; Copyright (2018) WILEY-VCH).

drogels successfully achieves the aim of maintaining the conductive-self healable bifunctionality after damages.

Besides the aforementioned self-healing polymeric hydrogels possessing electronic properties, those with magnetic properties have also stimulated research interests in the design and development of multifunctional SPHs. Due to the unique remote controllable property, these novel hydrogels are expected to be used in many practical applications, such as untethered soft robots, drug delivery and release, and tissue engineering and medical device.<sup>[55,56]</sup> The general method of preparing magnetic hydrogels was to incorporate a biocompatible magnetic material, *i.e.*  $\text{Fe}_3\text{O}_4$ , into hydrogel systems to afford the hydrogel magnetism, while simultaneously incorporating self-healing into hydrogel systems remains a big challenge.<sup>[57]</sup> We have reported a polymeric hydrogel that can deform on navigation in a magnetic field and spontaneously recover and fix the original shape with the assistance of near-infrared (NIR) irradiation. The hydrogel is obtained by embedding  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles into a poly(*N*-(2-hydroxyethyl) acrylamide)-gelatin double network structure. Specifically, with magnetic field mediated, the soft robots can do sit-ups, more complex hydrogel space station and hydrogel spacecraft that are able to be docked in the air, both of which can also be constructed. Moreover, upon the irradiation of NIR, the broken tail of hydrogel gecko could be

reconnected with the body, and the adhesive effect could be in accordance with the primal hydrogel gecko which is not subjected to mechanical damage. The reversible coil-triple-helix transformation of gelatin imparts the hydrogel with shape memory and self-healing behaviors, because of the thermal-activated self-healing property specific to gelatin (as shown in Fig. 7).<sup>[58]</sup> This kind of polymeric hydrogel will promote the design and construction of novel smart polymer systems with synergistic functions. Meanwhile, Zhao *et al.* also adopted gelatin as one of the constituents to prepare a structural color hydrogel with magnetic- and photo-thermal responsiveness, which was comprised of gelatin, agarose and the magnetic nanoparticles of poly(4-styrenesulfonic acid-co-maleic acid) sodium salt (PSSMA) $\text{@Fe}_3\text{O}_4\text{@SiO}_2$  colloids.<sup>[59]</sup> The self-healing abilities of the hydrogel can be induced by the alternating magnetic field and NIR due to the magnetic response and light absorbing abilities of the magnetic nanoparticles. Except for these functions, pairing with the high biocompatibility and plasticity, these features indicate the versatile values of this kind of hydrogel in the biomedical field and cell engineering. The impressive work mentioned above implies the remotely controlled possibility of magnetic self-healing hydrogels, and inspires the fabrication of novel magnetic self-healing systems with great potential in various fields.





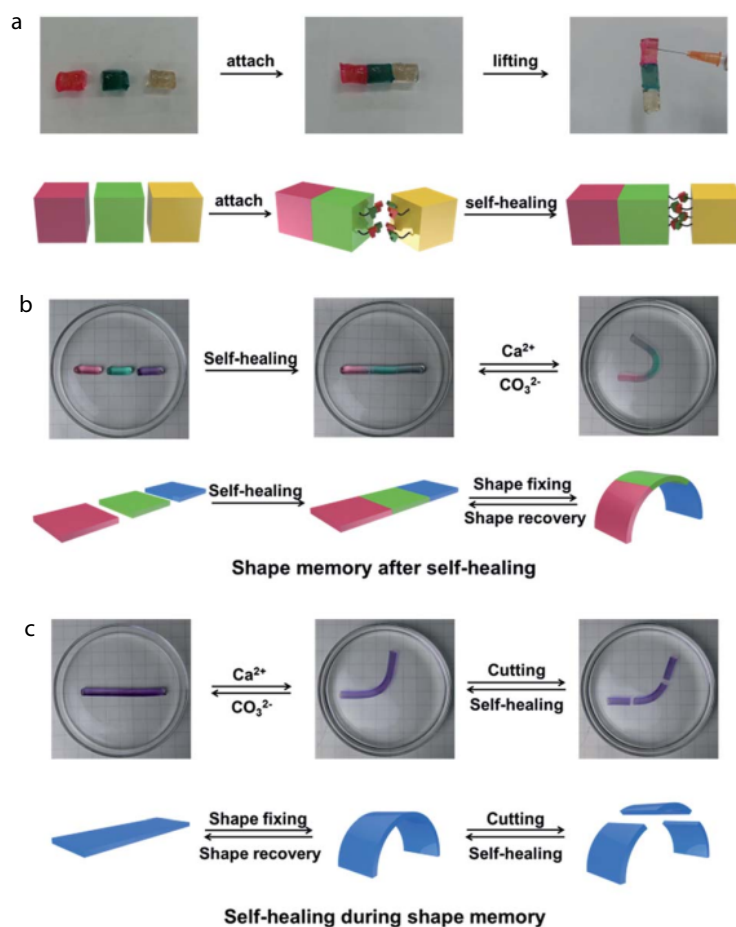
**Fig. 7** (a) The infrared images of the HG-Fe<sub>3</sub>O<sub>4</sub> hydrogel with 0 wt% and 1 wt% Fe<sub>3</sub>O<sub>4</sub> when irradiated by NIR for 0, 60, 120, 180, 240 s. (b) Schematic illustration of the self-healing mechanism. (c) A gecko's broken tail repair process. (d) Schematic illustration of a spacecraft joining with a space station in air. (e) A hydrogel spacecraft would approach a hydrogel space station under the guidance of magnetic field, and the two parts would connect together under the assistance of NIR (Reprinted with permission from Ref. [58]; Copyright (2021) WILEY-VCH).

### 3.1.3 Self-healing polymeric hydrogels with shape memory properties

For the considerations of completely restoring the original shape for SPHs, which is one of the major obstacles that may impede the application of self-healing hydrogels in stress-bearing area, considerable efforts are still needed to figure out an effective approach to this goal. To this end, shape-memory moieties, a kind of functional group that has the capability to “memorize” a preprogrammed temporary shape, and return to the original, stress-free shape upon a trigger *via* external stimuli, as a new candidate, were introduced into self-healing hydrogels to improve their mechanical performance.<sup>[60]</sup> Therefore, the integration of self-healing hydrogels with shape-memory properties may open a door for design and construction of novel multi-functional hydrogels, and show potential applications in many fields including biomedical, textile, flexible electronics, data encryption, etc.<sup>[61]</sup>

Except for the aforementioned thermal-induced shape memory behavior caused by the formation/disaggregation of gelatin triple helices,<sup>[58]</sup> there have been several successful attempts to employ the robust borate bonds for the fabrication of self-healable shape memory hydrogels.<sup>[24,62–65]</sup> One of the studies reported by our group proposed a facile and “off-the-shelf” method to construct polyacrylamide (PAAm)/PVA hy-

drogels with high shape memory fixity, efficient self-healing performance along with multiresponsive nature.<sup>[62]</sup> The chemically crosslinked PAAm network endows the hydrogels with permanent shapes, while the dynamic PVA-borax boronate ester bonds serve as the temporary crosslinks to stabilize the deformed shape of the hydrogels. Triggered by diverse stimuli such as acid and monosaccharides, the rupture of PVA-borax boronate ester bonds would help to recover its permanent shape. In addition, the developed phenylboronic acid group-functionalized hydrogels whose shape memory abilities and self-healing performance can be comparable to those of dynamic borate bonds-based hydrogels.<sup>[63–65]</sup> For example, we constructed a double network hydrogel consisting of PAAm, phenylboronic acid grafted alginate (Alg-PBA) and PVA, in which both the dynamic PBA-diol ester bonds and chelation of Alg-Ca<sup>2+</sup> endue the hydrogel with outstanding triple shape memory functionalities at both macro-scale and micro-scale.<sup>[63]</sup> As shown in Fig. 8, a noteworthy observation is the synergistic effect of self-healing and shape memory abilities, that is, shape memory capabilities can be retained after self-healing, meanwhile, the hydrogel can self-heal during the shape memory performance. These reported borate bonds have greatly enriched the type of self-healable shape memory hydrogels, and paved the way for the development



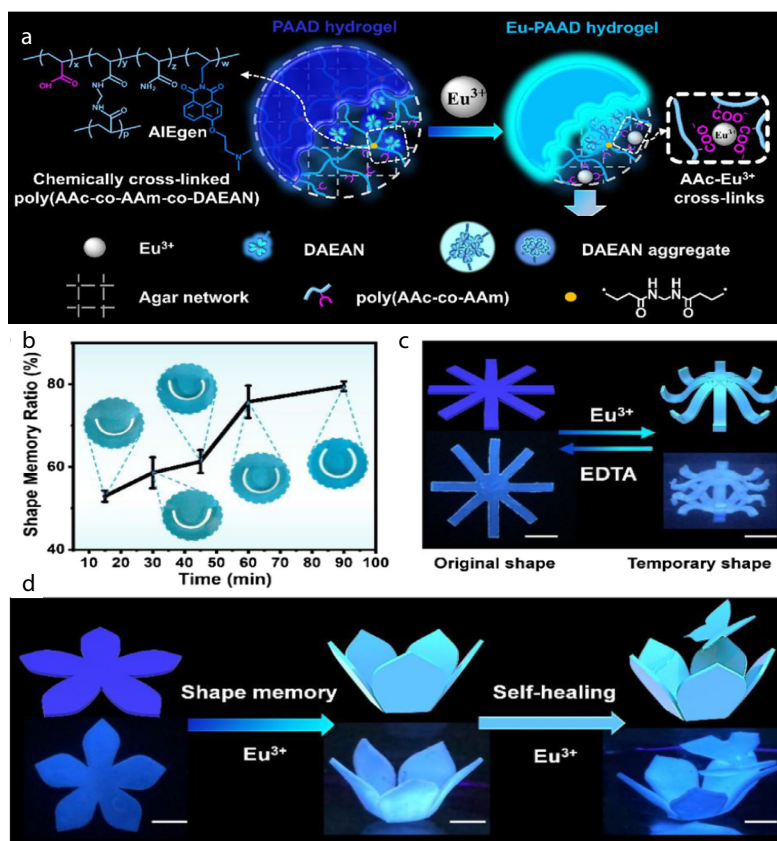
**Fig. 8** (a) Photographs and mechanism of the self-healing behaviour of the supramolecular hydrogel. Three pieces of hydrogel, where one was dyed with erioglaucine disodium salt (blue dye), and one was dyed with rhodamine B (red dye). The hydrogels are fused together and lift without fracture after fusion. (b) Shape memory after self-healing: a straight hydrogel strip was cut into three parts, and then self-healed at room temperature, the healed hydrogel was bent into a “U” shape and immersed in  $\text{CaCl}_2$  solution to fix the temporary shape, the hydrogel can recover to the original straight shape by extracting  $\text{Ca}^{2+}$  in  $\text{K}_2\text{CO}_3$  solution. (c) Self-healing during shape memory: a hydrogel strip was first fixed into a temporary shape, and then was cut into three pieces, after self-healing, the healed hydrogel can also recover to the original shape without breakage (Reprinted with permission from Ref. [63]; Copyright (2016) The Royal Society of Chemistry).

of multifunctional SPHs with shape memory properties.

Adapting a different strategy, we fabricated another polymeric hydrogel, the self-healing and shape-memory properties stem from the dynamic and reversible  $\text{AAc-Eu}^{3+}$  coordination interactions (Fig. 9).<sup>[66]</sup> This novel hydrogel could be programmed to perform more complex 2D-to-3D shape memory behaviors while employing the lanthanide coordination to fix the given shapes. EDTA is generally used to induce the shape recovery from 3D to 2D by the dissociation of metal-ligand coordination. To demonstrate the self-healing property, a butterfly structure hydrogel is first prepared in the shape memory process, followed by adhering it with a flower hydrogel *via* self-healing process in an aqueous  $\text{Eu}^{3+}$  solution, and the fabrication of the complex butterfly-on-flower-type 3D hydrogel structure is thus obtained. Furthermore, carboxymethyl chitosan (CMC), a derivative of chitosan, characterized by abundant hydrogen bonding, coordination active groups, excellent metal chelation and pH-dependent solubil-

ity, has often been considered as an alternative candidate for coordination with metal ions. Accordingly, it is obvious that the dynamic metal-ligand coordination provides new insight into preparation of self-healable shape memory hydrogels.<sup>[67,68]</sup>

Fei *et al.* succeeded in creating a thermo-healable hydrogel from covalently crosslinked PAAm and ionically crosslinked carrageenan.<sup>[69]</sup> This double network hydrogel is capable of being completely healed by the short treatment at 70 °C, since carrageenan generally melts at a mild temperature below 70 °C and gels *via* ionic association of double helix units, the feature of which renders the self-healing behaviors that quickly occur at mild temperatures. More interestingly, the shape-memory property of the hydrogel is embodied that it still preserves the stretched state upon stretching and drying, then quickly shrinks back to the original shape upon wetting. As shown in Fig. 10, a light-healable strong hydrogel with light-controllable shape memory property was reported,



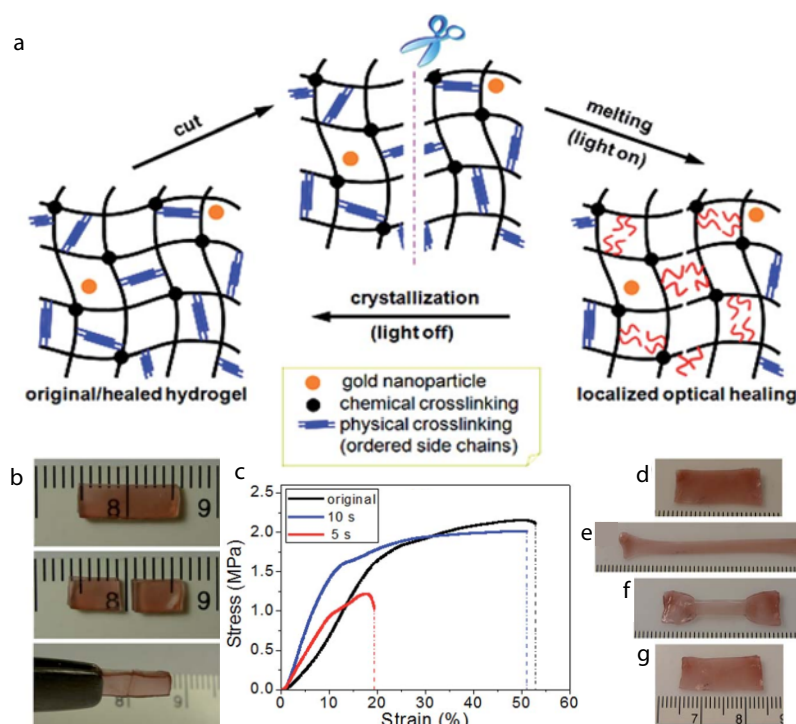
**Fig. 9** (a) Illustration of Eu-PAAD hydrogel and its molecular structure. (b) Shape fixity ratios of the PAAD hydrogel at different shape memory times in aqueous  $\text{Eu}^{3+}$  solution (0.1 mol/L) at 25 °C. (c) Fabrication of a 3D cuttlefish-shaped hydrogel structure by starting with one tailored 2D hydrogel piece *via* shape memory. (d) Fabrication of the complex 3D hydrogel structure (butterfly perching on the flower) by starting with two tailored 2D hydrogel pieces via the combination of shape memory and self-healing abilities at room temperature (photos taken under 365 nm illumination). Scale bars in digital photos are 1 cm (Reprinted with permission from Ref. [66]; Copyright (2021) WILEY-VCH).

which was prepared by stearyl acrylate (SA), *N,N*-dimethylacrylamide (DMA) and *N,N*-methylenebisacrylamide (MBA) with a small amount of gold nanoparticles (AuNPs, 0.05 wt%).<sup>[70]</sup> A significant healing effect can be achieved just within a 10 s laser exposure, with the almost complete recovery of the hydrogel's original mechanical properties, because of the photothermal effect induced reversible melting-crystallization phase transition of the hydrophobic associated SA chains. Likewise, this mechanism is also favor of the appearance of light-controlled shape-memory behavior of the AuNP-containing hydrogel. Another remarkable work that a novel kind of PVA hydrogels containing the light active polydopamine particles (PDAPs) can not only achieve rapid shape recovery but also possess efficient self-healing properties under NIR light exposure in a short time, was also presented.<sup>[71]</sup> The PVA-PDAPs composite hydrogels present a healing efficiency of 92% after 30 s of irradiation by NIR, as a result of the reformation of hydrogen bonds between PVA and PDAPs. As there are two reversible crosslinking networks coexisted in the hydrogels including hydrogen bonding and crystallization, the fixed phase is formed by the physically crosslinking network between PVA and PDAPs, while the reversible phase is composed of PVA crystallization. Due to the excellent photothermal effect of PDAPs, the composite hydrogels can thus display a NIR-assisted shape memory behavior that enables

the hydrogels to be reprogrammed and to recover repeatedly. Given the fact that a large number of multifunctional SPHs with shape memory properties emerge in recent years, more research efforts are highly expected to develop new-type self-healable shape memory hydrogels with more plentiful functionalities and promising uses.

### 3.2 Mechanically Robust Self-Healing Polymeric Hydrogels

The impressive advances mentioned above have enormously expanded the spectrum of SPHs, however, these systems are insufficient in terms of mechanical properties that would hamper their application. Due to the requirement of practical application, to simultaneously endow the hydrogels with good mechanical performance and efficient self-healing properties has attracted increasing attention, especially in the fields of tissue engineering, wound dressings, surgical sticky bandages, soft robotics and machinery, *etc.*<sup>[72,73]</sup> Considering the issues of the inherent compromise between the dynamic healing and mechanical strength, recent design and construction of mechanically robust self-healing polymeric hydrogels is still inevitable to confront some problems, because weak interactions benefit self-healing, yield soft materials, whereas strong interactions afford robust materials, precluding self-healing.<sup>[74]</sup>

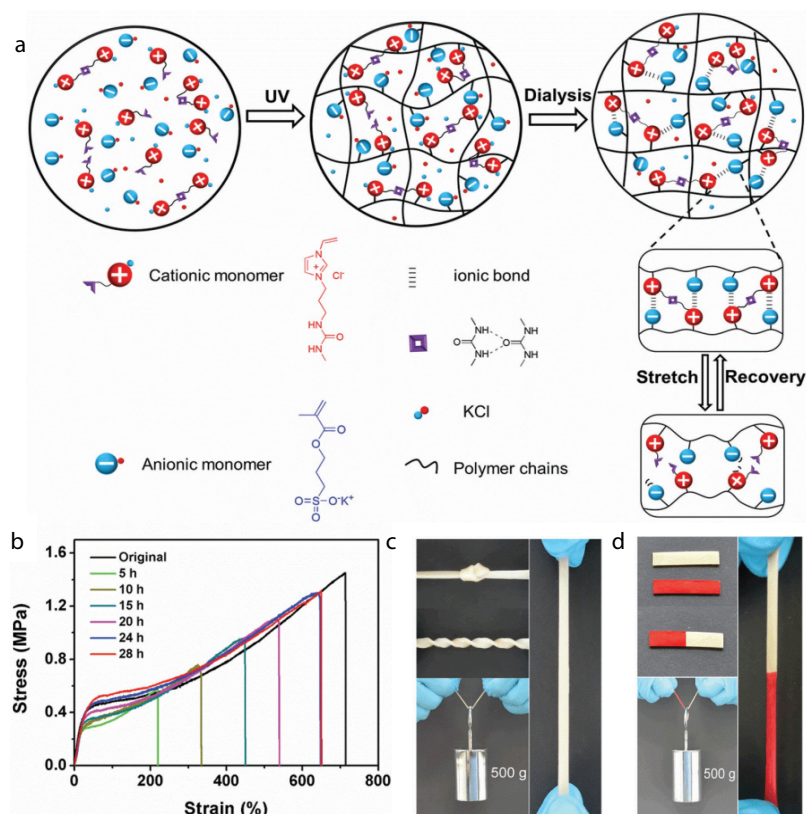


**Fig. 10** (a) Schematic illustration of a light-healable strong hydrogel based on a photothermally induced melting-crystallization phase transition of the physical crosslinks. (b) photographs that visually show the healing behavior; (c) stress-strain curves for the original and optically healed hydrogels with two short laser (0.72 W) exposure times at room temperature; (d) Light-controlled shape-memory behaviour of the hydrogel: photographs of a hydrogel in its original shape, (e) the temporary shape obtained by stretching the sample to  $\sim 100\%$  strain at  $70\text{ }^{\circ}\text{C}$  in a water bath followed by cooling to room temperature, (f) selective shape recovery by exposing the two end areas (about  $2/3$  of the sample) to the laser (0.32 W), and (g) fully recovered permanent shape after laser exposure of the central part of the sample (Reprinted with permission from Ref. [70]; Copyright (2014) The Royal Society of Chemistry).

Incorporation of the noncovalent sacrificial bonds is an advantageous strategy that has been widely employed for enhancing the mechanical strength of hydrogels, due to their capability to efficiently dissipate a large amount of energy through reversible bond rupture.<sup>[75]</sup> Sun *et al.* employed a one-step random copolymerization of positively charged imidazolium-based ionic liquid (IL) monomers containing urea groups (urea-IL) and negatively charged 3-sulfopropyl methacrylate potassium salt (SPMA) monomers, followed by dialysis in water for 3 days. The resulting P(urea-IL<sub>a</sub>-SPMA<sub>b</sub>)-*x*d polyampholyte hydrogels present a tensile strength and toughness of 1.3 MPa and  $6.7\text{ MJ}\cdot\text{m}^{-3}$ , respectively, as well as strain at break of 720% (as shown in Fig. 11).<sup>[76]</sup> The sacrificial bonds formed by hydrogen-bonding interactions between urea groups account for the successful fabrication of mechanically robust hydrogels. While the electrostatic interactions between imidazolium and sulfonate groups combined with hydrogen-bonding interactions make the hydrogel automatically heal at room temperature for 24 h with a healing efficiency of  $\approx 91\%$ . Moreover, the other fascinating properties of good resilience and satisfactory conductivity can also be found for these polyampholyte hydrogels. Another autonomous self-healing hydrogel based on Glycogen (Gly/PAAc-Fe<sup>3+</sup>) was fabricated by strategically programming a pervasive network of sacrificial metal-ligand interactions.<sup>[77]</sup> The hydrogel exhibits extraordinary mechanical properties with a fracture tensile stress and a compression stress of 0.4 and 32 MPa, re-

spectively, as well as a high fracture energy of  $3.5\text{ MJ}\cdot\text{m}^{-3}$ . In addition, hydrogel healed for 24 h at room temperature without any external stimuli shows an optimum healing of 83% recovery in stress relative to the original uncut hydrogel sample. The dual physically cross-linked networks *via* dynamic metal-ligand interactions explain the outstanding mechanical properties, and an excellent self-healing efficiency. The PAAm/PAAc hydrogel cross-linked by Fe<sup>3+</sup> carboxyl coordination bonds has also demonstrated that metal-coordination mediated physical hydrogels exhibit high strength/toughness and self-healing effect.<sup>[78]</sup> It is apparent that the noncovalent sacrificial bonds provide a generic approach to designing and constructing mechanically robust self-healing polymeric hydrogels, and establish a great foundation for bridging the high mechanical performance and self-healing properties.

Compared to covalent bonding, noncovalent bonding behaves the weaker and reversible nature of interactions, thus, the autonomous self-healing hydrogels fabricated by the single noncovalent bond generally exhibit poor mechanical properties.<sup>[11]</sup> So other approaches for design and construction of SPHs with extraordinary mechanical performance are centered on the integration of covalent bonds and noncovalent bonds, thereby introducing the superiorities of structural stability and higher mechanical strength into autonomous self-healing hydrogels.<sup>[11]</sup> A remarkable work proposed by Zhao *et al.* was inspired by the curing of marine mussel

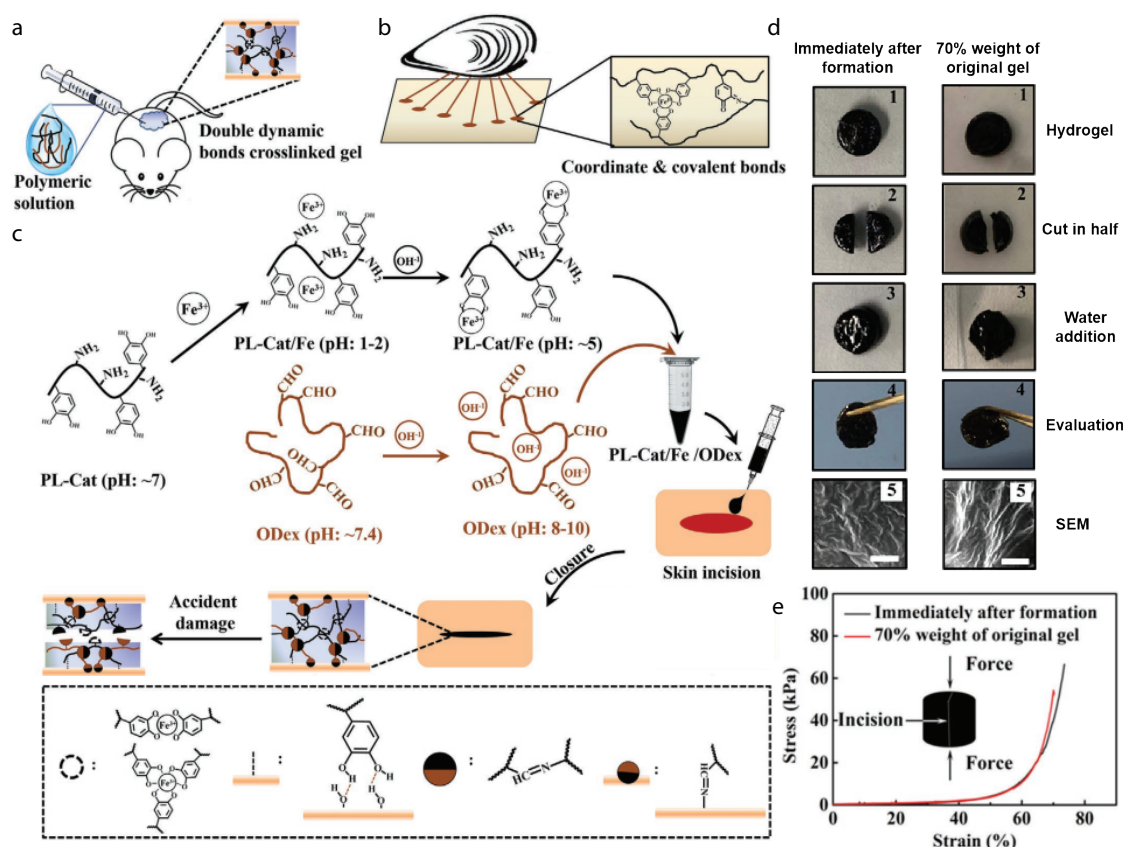


**Fig. 11** (a) Schematic illustration for the synthesis and structure of the P(urea-IL<sub>3</sub>-SPMA<sub>3</sub>)-*x*d polyampholyte hydrogels. (b) Stress-strain curves of pristine and self-healed P(urea-IL<sub>1</sub>-SPMA<sub>1</sub>)-3d hydrogels with different healing times. (c) Digital photos to demonstrate the high strength and toughness of the P(urea-IL<sub>1</sub>-SPMA<sub>1</sub>)-3d hydrogels: knotting, twisting, stretching, and lifting up a 500 g weight. The hydrogels have a width of 3 mm and a thickness of 1.7 mm. (d) Digital photos of dyed and undyed P(urea-IL<sub>1</sub>-SPMA<sub>1</sub>)-3d hydrogels being cut into two pieces and the two pieces with different colors being well healed at room temperature for 24 h. The healed hydrogel can be stretched and lift up a weigh of 500 g (Reprinted with permission from Ref. [76]; Copyright (2018) WILEY-VCH).

glue.<sup>[79]</sup> As shown in Fig. 12, they developed a bioadhesive with higher mechanical and good self-healing capacities formed by a three-component hydrogel architecture consisting of: (i) catechol-modified  $\epsilon$ -poly-L-lysine, (ii) oxidized dextran, and (iii) Schiff's base and catechol-Fe coordinate double-dynamic-bond crosslinked structure. The storage modulus and maximum compression stress could reach 7600 Pa and 80 kPa, respectively. Meanwhile, the self-healing efficiency of 91% could be realized by a drop of water ( $\approx 20 \mu\text{L}$ ) at room temperature, because the incorporation of water is helpful to activate the polymer chains at the incision interface. Another work carried out the solid-phase esterification reactions between hydroxyl-containing polymers and small carboxylic acids to prepare the mechanically robust SPHs, showing high tensile strength up to 11.19 MPa and efficient self-healing ability under ambient conditions, respectively, owing to the strong H-bonding and chemical ester bonds formed during the drying process.<sup>[80]</sup> Besides, the dynamic Schiff-base/hydrogen bonds,<sup>[81,82]</sup> Diels-Alder/metal-coordination bonds,<sup>[83]</sup> borate-ester/hydrogen bonds,<sup>[84]</sup> and acylhydrazone/multiple hydrogen bonds<sup>[85]</sup> play the same role in hoisting mechanical performance and offering self-healing capacities for hydrogels. More research interests and efforts are highly expected in this construction strategy.

Nanoparticulate fillers such as silica nanoparticles, clays,

and graphene oxide have been introduced into polymer materials to form nanocomposite hydrogels, wherein the fillers are not just dispersed into the hydrogel networks, but act as multifunctional crosslinking sites to obtain tough hydrogels; these approaches have aroused special interests owing to the obtained exceptional mechanical properties and simple preparation process.<sup>[86,87]</sup> For example, we successfully fabricated a healable, stable, and mechanical robust nanocomposite hydrogel, which was developed by using a PAAc network containing a new multifunctional macrocrosslinker, poly(2-dimethylaminoethyl methacrylate) brushes modified silica nanoparticles (SiO<sub>2</sub>@PDMAEMA).<sup>[74]</sup> The hydrogel presents tough performance that can withstand high deformation in compression without obvious damage, and can be stretched to more than 15 times then recover to its initial state, which benefit from the SiO<sub>2</sub> nanoparticles that play a role in dissipating energy. Additionally, the sample can be stretched as long as the original sample after 12 h of self-healing, which indicates the nearly 100% healing efficiency that derives from the electrostatic interactions between cationic PDMAEMA and anionic PAAc. Besides, the incorporation of lignin, *i.e.*, a kind of polyphenol bio-macromolecule with 3D network structure and antioxidant activity, can also effectively improve the mechanical and self-healing properties of poly(ionic liquids) hydrogels with the increase of lignin content, be-



**Fig. 12** (a)–(c) Schematic representation of the design strategy of the bioinspired, dynamic bonds crosslinked hydrogel bioadhesive capable of closing wounds. (d) Water-assisted self-healing. Left panel: After immediate formation. Right panel: After drying in the oven for 30 min (total weight was reduced to 70 % of initial weight). 1: Complete formation of the gel. 2: The gel was cut in half. 3: The gels were put together and a drop of water was added around the incision. 4: Photograph of gels after self-healing. 5: SEM photos after self-healing. The diameter of the hydrogel is about 8.5 mm. Scale bar in SEM photos: 150  $\mu\text{m}$ . (e) Compression curve of gels after self-healing (Reprinted with permission from Ref. [79]; Copyright (2020) WILEY-VCH).

cause of the dynamic ionic bonds formed by the large number of positive ions of poly(ionic liquids) and negative ions of lignin.<sup>[88]</sup> This kind of hydrogel dressing with excellent properties offers new opportunities for efficient skin wound care and management.

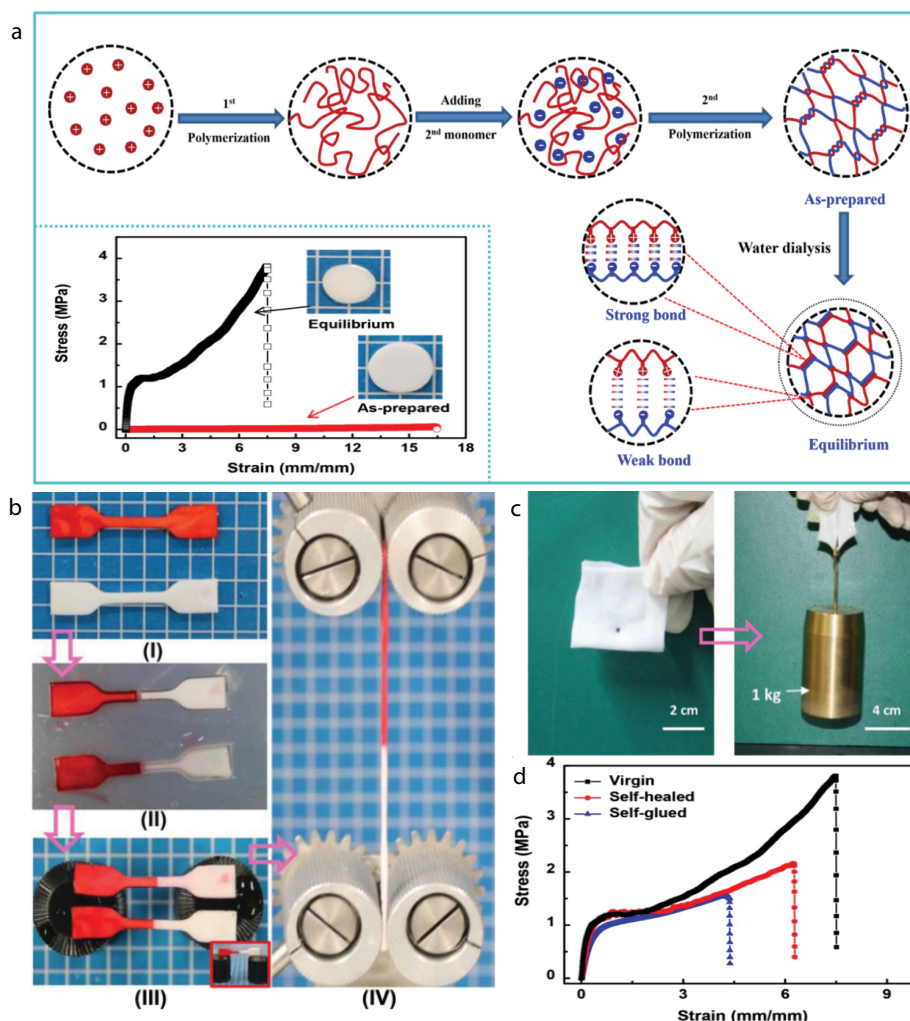
Polyion complexes (PIC) with a wide strength distribution are worthy of special note that they may provide dynamic crosslinking of an extremely wide lifetime scale. The strong, long lifetime bonds among them function as the permanent crosslinking, imparting elasticity, whereas the weak, short lifetime bonds serve as reversible crosslinking that break and reform at deformation to dissipate energy. Based on these knowledge, Gong *et al.* reported a new class of physical hydrogel which consists of oppositely charged polyelectrolytes, *i.e.* 3-(methacryloylamino) propyl-trimethylammonium chloride (MPTC) and sodium *p*-styrenesulfonate (NaSS).<sup>[89]</sup> The structure, having a double-network feature, renders the high strength and toughness of the as-prepared hydrogel (PMPTC/PNaSS). As shown in Fig. 13, the hydrogel shows a tensile strength of 3.7 MPa after dialysis in water. Owing to the reversible ionic bonds and saline softening effect, the hydrogel after 12 h healing time exhibits 66% repair at ambient condition with the aid of saline solution. Polyampholytes bearing randomly dispersed cationic and anionic repeat

groups, another kind of physical hydrogels along with multiple mechanical properties and self-healing properties, were also reported.<sup>[75]</sup> Apparently, this new class of physical hydrogels might open new avenue of tough hydrogels, and is critical to enable self-healing hydrogels with improved performance in mechanical properties.

#### 4. CONCLUSIONS, INSIGHTS AND CHALLENGES

In this review, we have portrayed a broad picture on recent advances on SPHs in terms of tunable mechanical properties and diverse functions. SPHs own many advantages compared to conventional hydrogels, endowed with extended life-time and enhanced durability due to the absence or decrease of irreversible damages. Although this field of study presents great promise, the future development still confronts some challenges that need to be addressed, including (i) enriching the variety of multifunctional SPHs; (ii) systematically researching the structure-property-function relationship for SPHs; (iii) promoting theoretical and simulated studies on the self-healing mechanism; (iv) developing assessment systems for quantitatively characterizing self-healing performance.

The research on multifunctional SPHs is still at its infancy, there are only a few classifications that can well present the



**Fig. 13** (a) Schematics of preparation of PIC hydrogels. (b) Self-healing behavior of the PMPTC/PNaSS hydrogels assisted by 3 mol/L NaCl solution. (I) Two pieces of virgin PIC hydrogels, one of them is dyed by Congo red; (II) The cut samples were reattached by embedding the two cut pieces in a silicone rubber mold with the same size of the sample. Before reattaching, the cutting surfaces of the samples were dipped in 3 mol/L NaCl solution for 2 min; (III) the self-healed samples after 12 h healing time; (IV) photograph demonstrating the large deformation of self-healed samples. (c) The sample shows notch-insensitivity as demonstrated by the suture test. A hole is made in the hydrogel, using a sharp awl, and a 1 kg weight is hung to the gel via the hole. (d) Stress-strain curves of the virgin, self-healed, and self-glued bulk samples (Reprinted with permission from Ref. [89]; Copyright (2015) WILEY-VCH).

multifunctional collaboration of self-healing and functionalities, and therefore, another future research trend prioritized is to enrich the variety of multifunctional SPHs with an emphasis on new applications. Up to date, many emerging luminescent materials (such as luminescent nanoclusters) and conductive materials (such as MXene) are worthy of being incorporated into SPHs.<sup>[90,91]</sup> Also, other unique functions, e.g. 3D/4D printability, anti-freezing properties, adhesive properties and sol-gel transition properties, etc, can allow the SPHs to be used as new classes of soft smart materials.

As the field of SPHs is an emerging one, the exploitation of new self-healing hydrogel structures is basically on a basis of trial-and-error, subsequently feeding back the data of property characterization, followed by structure modification according to the data. This complex procedure is mainly caused by the limited information and the undefined understanding of fundamentals in structure-property-function relationship

of SPHs. Therefore, introducing materials simulation into design and construction of SPHs is becoming one of the future research priorities in the development of SPHs, which is conducive to elaborately designing the accurate materials models to further establish rationale design of the materials with pre-determined functionality. Driven by the desire for systematic studies of hydrogels structure-property-function relationship, a computation method to simulate the properties including a self-healing property and tunable mechanical performance for various hydrogels is expected to facilitate screening/selecting specific structure for specific application, then endowing the structure with specific functions.

Grasping the mechanism of self-healing plays a crucial role in synthesis and optimization of SPHs. Unfortunately, except that Hui and co-authors put forward a 3D finite strain constitutive model to model the dynamic self-healing of gels,<sup>[92]</sup> there are few related researches about the theories and simu-

lations of self-healing mechanism, especially for hydrogels. Actually, the development of theory with the aid of simulation of self-healing mechanism specific to hydrogels would lay a solid foundation for further growth in this field. Research on this issue should be encouraged and expected.

Although a large number of SPHs with high performance have been obtained, there seems no standard measurement used quantitatively to evaluate self-healing, which leads to the difficulty in making a comparison between different studies. It is thus of great concern to develop the quantitative assessments for self-healing performance *via in situ* and non-destructive testing.

These aforementioned opportunities and challenges facing the field of SPHs require interdisciplinary collaborative research varying from chemistry, biology, physics to engineering. We believe, with the further research of self-healing technology, the future shines bright for SPHs with unique functionalities, meanwhile, we also hope that this review is helpful to the further breakthrough and improvement for SPHs, thereby leading the booming development of this field.

## BIOGRAPHY

**Wei Lu** received his PhD degree in polymer chemistry and physics from Zhejiang University in China (2014). Soon afterwards he joined Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences. He was promoted to Associate Professor in 2017 and Professor in 2020. His current research is focused on the fabrication of multi-functional fluorescent polymeric materials for applications in chemical sensing and biomimetic actuators.

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