Recent Advances in Self-Healable Intelligent Materials Enabled by Supramolecular Crosslinking Design

Jize Liu, Xinkai Li, Xin Yang, and Xinxing Zhang

High-performance intelligent materials with unique stimulus-responsive properties are highly desired in the future as the rapid development of intelligent systems for Internet-of-Things applications. During their long service life, the irregularity in external stimuli and repetitive motions always result in unavoidable permanent damages, where the self-healing ability inspired by skin is indispensable and highly attractive. However, the introduction of supramolecular networks to achieve self-healing ability based on reversible dynamic noncovalent bonds usually leads to relatively low strength, while the conflict between high mechanical properties and high self-healing efficiency is still a great challenge. Moreover, the lack of efficient interfacial interaction between functional layer and self-healable polymer matrix leads to a permanent function loss during the healing of matrix. Herein, a brief overview of self-healable sensors and actuators based on recent strategies including multiple noncovalent interactions, covalent–noncovalent interactions, and interfacial supramolecular crosslinking is presented. The advantages and applications of high-performance self-healable sensors and actuators enabled by interfacial supramolecular crosslinking are discussed emphatically, and the conclusions and outlooks of self-healable intelligent materials are presented.

1. Introduction

Digital technology and intelligent systems are transforming our lives with the Internet of Things (IoT). Intelligent materials such as sensors and actuators as a result have attracted great concerns in the past decades for their applications in the future with the potential growth of intelligent lifestyles.[1–3]Attributed to their unique stimulus-responsive characteristics, intelligent materials always play an important role in the achievement of intelligent systems.[4,5] However, the irregular external stimulus and repetitive motions of stimulus-responsive materials during their long service life result in unavoidable permanent damage and function loss, which may lead to an unexpected system failure and unpredictable consequences. Therefore, inspired by skins which can heal spontaneously from mechanical damage, the self-healing ability plays an important role in the long-term stable service of intelligent materials and devices under complex applied conditions.[6,7]

Existing literatures have provided valuable references for the design and fabrication of self-healable materials based on hydrogen bonding, metal–ligand coordination, ionic and host–guest interaction, etc.[8–10] For example, Leibler and co-workers presented molecules associating together via hydrogen bonds, which can repair from damage spontaneously by simply bringing fractured surfaces together at room temperature.[11] Aida and co-workers reported low-molecular-weight polymers cross-linked by dense hydrogen bonds with robust mechanical properties, which can heal by compression without heating.[12] Clearly, the introduction of noncovalent network endows the materials with desired self-healing ability and efficiency due to their reversible reconstruction characteristic under stress and damage.[13,14] Compared with covalent bonding, supramolecular networks based on these dynamic noncovalent bonds exhibit a better durability but relatively low strength, which usually results in poor mechanical properties.

For the construction of desired stimulus-responsive intelligent materials, functional fillers such as graphene, carbon nanotubes (CNTs), and metal nanofillers are typically important components of self-healable intelligent materials.[15–17] In general, functional inorganic materials are introduced into self-healable polymer matrix for the achievement of desired function by spraying, printing, blending, etc.[18–21] Given the fact that the inorganic functional network exhibits a poor self-healing property, the lack of efficient interfacial interaction between fillers and polymer matrix leads to a permanent function loss during the healing process of matrix. Moreover, self-healable intelligent materials based on healable matrix without effective nanostucture and interfacial design require a high additive amount of functional fillers, thus resulting in unsatisfied mechanical properties and high cost, which hinder their further applications in the future.[22,23] To date, it is still a great challenge to develop intelligent materials with both mechanical and functional self-healing ability, as well as robust mechanical properties.
This progress report mainly focuses on the design, performance, and applications of recent self-healable sensors and actuators enabled by supramolecular crosslinking design. Especially for interfacial supramolecular crosslinking design, which exhibits a desired stability and durability under long-term external stimuli with an enhanced mechanical property due to their effective interfacial interaction between assembled fillers network and polymer matrix. This article intends to provide some recent advances in high-performance self-healable sensors and actuators based on multiple noncovalent interactions, covalent–noncovalent interactions, and interfacial supramolecular crosslinking design, demonstrate the principles and advantages of interfacial crosslinking strategy and discuss outlooks on opportunities and challenges of high-performance self-healable intelligent materials. Recent advances in self-healable sensors and actuators are briefly described at the beginning. Then, advantages and applications of high-performance self-healable sensors and actuators enabled by interfacial supramolecular crosslinking are introduced emphatically. Finally, the conclusions and outlooks are discussed.

2. Recent Advances in Self-Healable Materials

Self-healing materials have attracted a great interest for their skin-like ability to recover from damage. The supramolecular interaction design is the core issue for the achievement of high-performance self-healable materials, in which the supramolecular network is destroyed and dissipates the stimulus energy under external stimuli and rebuilds after withdrawing the applied stimulus. However, for the fact that noncovalent interaction is weaker than covalent bonding, the mechanical properties of the resulted self-healable sensors and actuators are always unsatisfied. How to improve the mechanical properties while maintaining desired self-healing performance is widely concerned.\[24–26\]

2.1. Self-Healable Materials Based on Multiple Noncovalent Interactions

Due to the unsatisfied mechanical properties of intelligent materials based on single noncovalent interaction design, multiple noncovalent networks have recently been designed and achieved in self-healable intelligent materials.\[27,28\] Compared with materials based on single noncovalent network, it has been confirmed that multiple noncovalent networks with several different intensities of interaction exhibit better mechanical properties such as higher strength, notch-insensitive higher stretchability and higher toughness, which are highly desired for the achievement of robust self-healable intelligent materials.\[29–31\]

Several different multiple noncovalent network designs have recently been presented and applied in self-healable intelligent materials. Bao and co-workers reported a new class of polymeric material crosslinked through rationally designed multiple hydrogen bonding interactions with different strength, as shown in Figure 1a. A supramolecular polymer film constructed via a mixture of strong and weak crosslinking hydrogen bonds was designed and fabricated through a one-pot polycondensation reaction. The resulting polymer exhibits desired mechanical

![Figure 1. a) Schematics of a stretched i) polymer film, ii) notched film, and iii) healed film as well as the possible hydrogen bonding combinations for strong bond and weak bond, respectively. b) Self-healing process of the supramolecular polymer film under water and a comparison of this work to recent works in synthetic stretchable and tough materials. a,b) Reproduced with permission.\[32\] Copyright 2018, Wiley-VCH. c) A comparison of the self-healing efficiency and tensile strength between single noncovalent interaction, multiple noncovalent interaction, and covalent-noncovalent interaction.\[32,37,41,68–82\]
properties (≈1.5 MPa) and self-healing performance, e.g., high stretchability (1200%), high toughness (12 000 J·m⁻²). Moreover, the materials exhibit an autonomous self-healing ability even in artificial sweat, as shown in Figure 1b. Compared to the reported works at same period, the introduction of the multiple noncovalent interaction endows the materials with desired mechanical properties, achieving a great balance between fracture energy and maximum strain at break.[32]

In another work, a substrate material designed for self-healing capacitive sensors based on combining dynamic metal-coordinated bonds with hydrogen bonds together in a multiphase separated network was reported. The obtained self-healable sensor exhibits high tensile strength that break (≈1.8 MPa), large fracture strain (≥900%), and 98% of self-healing efficiency (48 h at 25 °C).[33] A series of recent works confirmed that compared with single noncovalent network, self-healable intelligent materials based on multiple noncovalent interactions exhibit higher mechanical properties and robustness due to their intricate interactions design.

To better demonstrate the effect of the interaction design, a comparison of self-healing efficiency and tensile strength between single noncovalent interaction, multiple noncovalent interaction, and covalent–noncovalent interaction are presented in Figure 1c. Usually, self-healable materials based on single noncovalent interaction exhibit a high self-healing efficiency but low tensile strength, which may be attributed to the real-time dynamic fracture and reconstitution of the noncovalent interaction. Multiple noncovalent interaction designs based on the combination of a series of noncovalent interaction endow the materials with enhanced mechanical properties. However, for the fact that the molecular structure and interaction design for multiple noncovalent crosslinking network are more complex, the self-healing efficiency of the obtained materials is sometimes lower. Therefore, more elaborate materials design based on the combination of different noncovalent interaction is still attractive, which may lead to both high mechanical properties and high self-healing efficiency at the same time.

2.2. Self-Healable Materials Based on Covalent-Noncovalent Interactions

Another strategy for high performance self-healable sensors and actuators is constructing covalent–noncovalent interactions in polymer matrix.[34–36] The combination of two networks in a hybrid material has been reported for the design of high-performance self-healable materials. The synergistic effect of irreversible covalent crosslinking and reversible noncovalent interaction endow the materials with fascinating properties and improved mechanical properties. The combined network exhibits a satisfied self-healing performance and robust mechanical properties, which is an ideal matrix for self-healable intelligent materials.[37–40]

Zhang and co-workers reported a new strategy to construct tough and multi-recyclable cross-linked supramolecular polyureas by incorporating noncovalent bonds into main-chains (Figure 2a). The obtained materials exhibit remarkable solvent resistance and outstanding mechanical properties with superior toughness of 124.17 MJ m⁻³. Moreover, the mechanical properties recover more than 95% of original properties even after five generations of recycling processes, displaying excellent multiple recyclability. The superior toughness, high transparency, and excellent multiple recyclability (Figure 2b,c,d) has been achieved due to the construction of effective covalent–noncovalent network (>30 MPa, and high-temperature recycling process is needed). The work provides a facile and general method for high-performance recyclable materials, which greatly benefit the design and fabrication of robust self-healable intelligent materials in the future.[37]

As another valuable example, Zhang et al. reported a biopolyester based on an elaborately designed covalent–noncovalent network. The obtained self-healable actuators exhibit a series of desired properties such as straightforward manufacturability at low ambient temperature (≤35 °C), fast and stable response, robust mechanical properties, and excellent self-healing ability. As shown in Figure 3, a biopolyester with hydrogen bonding

![Figure 2](image)

**Figure 2.** a) A schematic diagram of the chemical design and recycling process based on the strategy of incorporating noncovalent bonds. b) Photographs for demonstrating the recycling process (scale bar: 1 cm). c) Stress–strain curves after multiple generations of recycling. d) Plot of recycle number versus toughness after recycling and other reported recyclable cross-linked thermosets.[83–92] a–d Reproduced with permission.[37] Copyright 2020, Wiley-VCH.
and covalent bonding interpenetrating network was designed and achieved, and the corresponding hygroscopic actuator exhibits excellent mechanical property and high self-healing efficiency. \[43\] Such self-healable intelligent materials based on covalent–noncovalent interaction design exhibit high stretchability and repeatability, desired mechanical strength, and excellent self-healing ability. As shown in Figure 1c, self-healable materials with covalent–noncovalent interaction exhibit a desired self-healing efficiency and tensile strength, which may extend new possibilities in the design and applications of intelligent materials. In the future, how to design self-healable materials with high mechanical performance and high self-healing efficiency based on covalent–noncovalent interaction which can spontaneously repair at room temperature still remains attractive.

2.3. Self-Healable Materials Based on Interfacial Supramolecular Crosslinking

Self-healable intelligent materials based on multiple noncovalent interaction and covalent–noncovalent interaction have achieved some desired properties; however, there are still some challenges. For most sensors and actuators based on self-healable matrix and functional fillers, there is an irreconcilable conflict between high mechanical performance and high self-healing efficiency, whereas the room temperature, spontaneous and real-time self-healing is still attractive. Moreover, the lack of interfacial control and nanostructure design always leads to a permanent function loss during the healing of matrix, hindering their long-term stable operation in intelligent systems in the future.

Considering that functional fillers are usually needed in the design of intelligent materials, the introduction of noncovalent interactions between fillers and polymer matrix may open up new opportunities in the achievement of high-performance self-healable intelligent materials. For the construction of interfacial supramolecular crosslinking, fillers and polymer matrixes are usually modified separately and corresponding groups are introduced; then the desired supramolecular interactions are mainly concentrated at the interface during the assembly process. Contrast to others reported strategies, the collective effect of noncovalent interactions at the interface of fillers and polymer matrix produces a strong adhesive force, endowing the obtained self-healable materials with a series of advantages such as enhanced mechanical properties and excellent functional stability.\[42–47\]

How to construct an efficient interaction between polymer matrix and functional network is the key topic of the design and achievement of self-healable intelligent materials. A highly sensitive and self-healable strain sensor based on interfacial hydrogen bonding interaction and nanostructured conductive network has been presented as shown in Figure 4a.\[48\] Nanohybrids of CNTs and carboxyl cellulose nanocrystals were used to construct interfacial interactions with chitosan-decorated epoxy natural rubber matrix, the reversible hydrogen bonds endow the obtained sensor with extremely fast (<15 s) and repeatable self-healing ability and high healing efficiency (93% after the third healing process as demonstrated in Figure 4b,c). In another work (as shown in Figure 4e,f), interfacial supramolecular crosslinking based on metal–ligand coordination exhibits a higher self-healing efficiency (≈100%). Contrast to other reported self-healable sensors, the samples (red stars) exhibit the highest self-healing efficiency within a very short time, which is of great significance to the long-term stable operation of intelligent systems.\[49\]

On the basis of interfacial interaction design, intelligent materials with different functional fillers and nanostructure design may achieve higher performances and more attractive characteristics. A novel self-healable multi-stimuli responsive supramolecular elastomer embedded with a 3D interconnected nanohybrids network has been demonstrated, as shown in Figure 5a.

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**Figure 3.** a) A schematic of chemical structure and network structure before and after crystallization-melting transition. b) Schematics of the self-healing mechanism, typical stress–strain curves of the original, first and second healed copolymer sample. c) Comparison of ultimate tensile strength and self-healing efficiency among different soft actuator materials.\[72,91–97\] Reproduced with permission.\[91\] Copyright 2019, Wiley-VCH.
The construction of the organized assembly network and the interfacial metal–ligand coordination cross-linking interaction resulting in enhanced mechanical properties (10 MPa, which is higher than most reported self-healable actuators) and excellent self-healing performance (98% of the self-healing efficiency) in both mechanical and actuating properties. In summary, due to the collective effect of the noncovalent interaction at the interface between polymer matrix and fillers, self-healable materials based on interfacial crosslinking strategy exhibit desired mechanical properties and self-healing efficiency. By adjusting the interaction design, high mechanical properties (10 MPa) and high self-healing efficiency (98%) have been...
achieved simultaneously, while the obtained materials can be spontaneously cured from damage at room temperature in a short time. In contrast to the reported works in Figure 1c and Table 1, the interfacial supramolecular crosslinking strategy endows the self-healable materials with desired properties, which may open up new opportunities for the design and fabrication of high-performance self-healable intelligent materials. In the future, more kinds of interfacial interaction design such as reversible-covalent interaction and multiple noncovalent interaction may bring more attractive properties for self-healable materials. Although the construction of effective interfacial supramolecular interaction is sometimes complex while more elaborate nanostructure design is needed, the strategy is still attractive for its irreplaceable advantages.

3. Self-Healable Intelligent Sensors and Actuators

For most intelligent materials, the irregular external stimuli and repetitive motions during their long service life always result in unavoidable permanent damages, where the self-healing ability inspired by skin is indispensable. How to design and fabricate high-performance intelligent materials with both mechanical and functional self-healing ability is always attractive. High-performance self-healable intelligent materials (take sensors and actuators as examples) based on noncovalent interactions have attracted great interests due to their unique stimulus-responsive properties and skin-like self-healing characteristic.[32,51–55]

3.1. Self-Healable Sensors

For self-healable strain sensors, conductive fillers are usually needed for the achievement of strain-sensing ability. A reported strategy is introducing functional layers onto self-healable polymer substrates; the thin conductive layer endows the composites with high sensitivity while the substrates own self-healing ability. For example, Haick and Huynh synthesized and assembled self-healing polymers and composites for a bendable and stretchable self-healing chemiresistor achieved by disulfide-cross-linked polyurethane and polyurethane/silver-nanoparticles composite. The obtained flexible self-healing device is sensitive to pressure, temperature, and volatile organic compounds. The desired healing efficiency (function healing times of >30 min) endows the sensor with excellent robustness, which can survive after several times of cutting and the sensitivity only slightly decreases (<10%) after 6 months.[56] Yan et al. reported supramolecular polymer materials with excellent stretchability and self-healing behavior, while the gold thin-film electrode deposited on the self-healable substrate retains its conductivity and combines high stretchability (40%). The composites exhibit a series of desired properties such as fracture/notch insensitivity and self-healing ability, indicated that the functional thin-film electrodes can be significantly enhanced by combining with designed high-performance self-healable substrate and good interfacial adhesion with the substrate.[57] For the intelligent functional devices, in addition to the excellent functionality, the functional recovery after damage-healing process and long-term stability are also important considerations. However, devices based on healable matrix and functional layers usually show a potential limitation for that the functional layer sometimes owns dissatisfactory self-healing ability.

Self-healable conductive polymer hydrogel also received a wide attention because of their high stretchability, excellent flexibility, and biocompatibility. For high-performance self-healable devices based on conductive polymer hydrogel, the sensitivity and anti-drying ability are usually the core issue. Norford and co-workers reported ultra-stretchable and self-healable sensors based on ionic κ-carrageenan/polyacrylamide double network fabricated by solvent-exchange strategy. The obtained hydrogel sensors exhibit high stretchability, fast response (0.27 s) and recovery time (0.3 s) and wide detection range (490%), while the introduced hygroscopic ethylene glycol and glycerol endows the hydrogel with both anti-drying ability and humidity sensing capabilities.[58] In another work, Park and co-workers presented a robustness and self-healable conductivity hydrogel realized by chemical/ionic cross-linked poly (acrylic acid) intercalated with physically cross-linked poly(vinyl alcohol). The obtained hydrogel exhibits high stretchability, high self-healing efficiency (greater than 80% after 24 h) and 0.14 S m−1 of ionic conductivity, which is electrically healable. The resulted strain sensor can detect mechanical folding and pressure changes independently when attached to a finger, which can undergo large deformation for more than 1000 times.[59] In the future, self-healable sensors based on polymer hydrogel with high mechanical properties

| Designed strategy | Reference number | Tensile strength | Maximum strain at break | Self-healing efficiency |
|-------------------|-----------------|-----------------|-------------------------|------------------------|
| Multiple noncovalent crosslinking | [32] | 1.7 MPa | 1700% | 78% |
| | [71] | 3.24–8.25 MPa | 20–60% | 63–87.9% |
| | [72] | 0.2 MPa | 10^2–10^4% | 90% |
| Covalent-noncovalent crosslinking | [73] | 13 MPa | 100–175% | 30% |
| | [41] | 3 MPa | 80–100% | 88% |
| | [74] | 0.63 MPa | 50–80% | 80% |
| | [37] | 34 MPa | 100–500% | 95% |
| Interfacial noncovalent crosslinking | [48] | 0.8 MPa | 500–600% | 93% |
| | [49] | ≈2 MPa | 1000–1350% | ≈100% |
| | [50] | 10 MPa | 500–600% | 98% |
| Coordinate bonding interaction | [75] | 500 KPa | – | 83% |
| | [76] | 0.08 MPa | 400–450% | 92% |
| | [77] | 1.4–2.5 MPa | 200–800% | 85–95% |
| | [78] | 0.6 MPa | 200–300% | 76% |
| Ionic bonding interaction | [79] | 0.5 MPa | 900–1000% | 90% |
| | [68] | 0.45 MPa | – | 95% |
| | [80] | 100 KPa | 1000–2500% | 81.6% |
| | [81] | 9 Mpa | 750–4000% | 10% |
| Hydrogen bonding interaction | [82] | 9.2 KPa | – | 99% |
| | [69] | 0.13–0.27 MPa | 400–1000% | 91–95% |
| | [70] | 0.086–0.85 MPa | 200–600% | 53–98% |
(including stretchability and tensile strength), desired robustness and high sensitivity exhibit a broad application prospects. Self-healable polymer composite with functional fillers is another effective strategy to fabricate high-performance and robust devices. However, the introduction of functional fillers without interfacial interaction sometimes leads to unsatisfied mechanical properties. Interfacial supramolecular interaction design has been proposed to fabricate high-performance self-healable intelligent materials, in which functional fillers take part in the self-healing process due to the introduction of interfacial interaction and greatly benefit the healing of function. For most stimuli-responsive materials, the functional performance is highly dependent on functional fillers (species, filling content, distributed morphology, etc.), where the nanostructure design of composites is the core issue.\[60\] The interfacial crosslinking strategy can be easily combined with elaborate nanostructure design which achieves a high-performance and high-functional healing efficiency simultaneously, exhibiting an attractive application prospect in the future.

To meet the requirement of long-term accurate detection of complicated daily human motion, sensors with high self-healing efficiency which can make accurate response to small strain are highly desired.\[61\]–\[64\] A self-healing sensor with tunable positive/negative piezoresistivity has been reported, where the interfacial metal–ligand coordination plays a core role in the achievement of self-healing ability and the construction of hierarchical functional assembly network (Figure 6a). Due to the special hierarchical structure design (including nanostructure and interfacial supramolecular network), the resulted sensor with/without a flexible yarn electrode exhibit a tunable negative/positive piezoresistivity, while exhibiting a fast and repeatable self-healing ability with high-healing efficiency at the same time. Because of the energy dissipation effect of the interfacial supramolecular interaction, the healed samples keep its flexibility, high sensitivity, and accurate detection capability after healing process and bending over 10 000 cycles. The self-healable sensor with tunable piezoresistivity based on interfacial metal–ligand coordination interaction exhibits wide potential applications for next-generation wearable electronics and intelligent systems.\[49\]

As shown in Figure 6b, sensors based on interfacial supramolecular crosslinking exhibit a desired function recovery due to the integrated design of healable composites and function. The responsive behaviors of the devices after damage-healing process is highly consistent with the behaviors before damage, endows the systems with excellent robustness to mechanical damage. In the future, more elaborate nanostructure and interfacial interaction design is still highly attractive—interfacial supramolecular crosslinking strategy may open up new opportunities for the design and achievement of high-performance self-healable intelligent materials. Moreover, the development and promotion of intelligent systems based on self-healable intelligent materials will be attractive. For example, in Figure 6c, human–machine interaction intelligent system has been demonstrated by developing a facial expression control system and an electronic larynx, which is prospected to provide long-term highly stable services for patients and the disabled in the future.\[48\]

3.2. Self-Healable Actuators

Stimuli-responsive soft actuators based on stretchable, robust, and self-healing materials have attracted a great interest, while

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**Figure 6.** a) Strain-sensing mechanism and piezoresistive properties of designed tunable negative/positive piezoresistivity sensors. Reproduced with permission.\[49\] Copyright 2018, Wiley-VCH. b) Current responses of the original and the healed sensors in the detection of human motions. c) Robot control system based on the self-healable strain sensors. b,c) Reproduced with permission.\[48\] Copyright 2017, Wiley-VCH.
it remains a formidable challenge to develop high-performance self-healable actuators. The most pressing challenges including slow response, low mechanical strength, and limited functionalities greatly hinder their further application. Moreover, for high-performance self-healable actuators, the potential function loss after damage-healing process may lead to the intelligent system failure during their service life.

A supramolecular design strategy is presented by Connal and co-workers; the introduction of benzylamine functionalized anthracene group and acid ether hydrogen bonds endows the materials with high strength, rapid self-healing ability (within 8 min), and fast light-driven shape morphing. The visible-light-driven and fast deformation both in wet (10 min) and dry states (10 s) has been successfully demonstrated, and the capability of being recyclable and reprogrammable has also been presented (Figure 7a). The design enables the materials and devices to be recycled and reprogrammed into different 3D objects, which is an important step forward to develop a novel light-controllable hydrogel. Photoactuators based on liquid crystal elastomers show photoinduced motions, which are also widely studied in the preparation and application of high-performance actuators. Flexible and stretchable actuators based on azopolymers exhibit good processability and photoinduced bending ability due to the photoinduced trans–cis isomerization of the azopolymers. As shown in Figure 7b, the stretched film bend toward the UV light source (bending angle 62°) after irradiation for 10 min, and bend away from the blue light source (changed back to the upright position after 50 s). The photoinduced reversible solid–liquid transitions provide a new strategy for designing actuators with good reprocessability and healing ability.

In another work, as shown in Figure 8a, a structurally transformable and mechanically self-healable humidity-responsive material has been presented. Due to the designed covalent–noncovalent network and 3D shapes, functions such as grasp, swing, close open and lift are successfully achieved within 30 s of the moisture absorption time. The actuation motility can be turned on and off many times without apparent fatigue; the bending angle and actuation time of each cycle keeps highly consistent with relative humidity. Moreover, the responsive behaviors keep consistent with the initial samples after damage-healing process, indicating excellent robustness and function healing ability. Due to the biocompatibility and transformability of the self-healable materials, the obtained actuator exhibit diverse practical applications in the future. A series of reported works about high-performance self-healable actuators have achieved apparent progress; however, higher mechanical properties and combination of multifunction is still highly attractive.

For devices based on interfacial supramolecular crosslinking strategy, the combination of fillers assembled network and interfacial interaction open up more opportunities in high-performance multi-stimuli responsive materials. The introduction of ferric oxide nanoparticles and the construction of the organized assembly network endow the materials with high photothermal efficiency (ηPT = 79.1%), high thermal conductivity (31.92 W m⁻¹ K⁻¹), and a superfast actuating response (near-infrared light: 0.44 s; magnetic field: 0.36 s). As shown in Figure 8b–d, the biomimetic actuator exhibits high photothermal efficiency, high thermal conductivity, and superfast actuating response to magnetic field. It is worth to notice that the responsive behaviors of the healed samples keep highly consistent with the initial samples after damage-healing process (even after healing for 20 times), indicating that the interfacial supramolecular crosslinking strategy endows the obtained actuators with excellent self-healing performance in both mechanical properties and function. A series of reported works have demonstrated that the interfacial supramolecular crosslinking design greatly benefits the long-term stable service of intelligent materials under complex applied conditions, offering a valuable design strategy of high-performance self-healable intelligent materials. In addition, in the future, efficient and digital materials design strategies and responsive prediction methods may greatly benefit the development and applications of advanced intelligent systems.

4. Conclusion

In summary, as the key part of intelligent systems, self-healing ability is indispensable for stimuli-responsive materials due to the inevitable irregularity external stimuli and repetitive motions. Recent advances about multiple noncovalent interactions and
covalent–noncovalent interactions have achieved some desired progresses, while there are still challenges including permanent function loss and the conflict between mechanical performance and self-healing efficiency. The interfacial supramolecular crosslinking strategy endows intelligent materials with a series of advantages such as enhanced mechanical properties, extremely fast and repeatable self-healing ability, high healing efficiency and excellent functional healing ability, etc. Moreover, the introduction of interfacial interaction can be easily combined with elaborate nanostructure design and achieve higher performance and more attractive characteristics, which exhibit a great potential application in various intelligent systems in the future.

5. Outlook

Self-healable intelligent materials have progressed rapidly in recent years. However, several challenges need to be addressed: 1) Conflict between high mechanical performance and high self-healing efficiency: Although recent works about self-healable intelligent materials have achieved many advances, the mechanical properties of these materials are still not satisfied enough in contrast to commercial covalently crosslinked materials. Therefore, it still remains an attractive target to simultaneously achieve higher mechanical properties and self-healing ability. 2) Advanced nanostructure and supramolecular interaction design: To meet the requirement of long-term application in complicated scenarios in the future, advanced nanostructure design and excellent function stability is still highly attractive. High performance, high robustness (both for mechanical properties and function) and easily prepared intelligent materials with more elaborate nanostructure, and efficient supramolecular interaction design are still highly desired. 3) Validation in intelligent systems and practical application scenario: The long-term stability of self-healable intelligent materials under complicated condition such as high/low temperature, acid/base solution, and outdoor degradation is still to be tested. In addition, the development and promotion of efficient and digital materials design strategies, responsive prediction methods, and relative integrated intelligent systems will be attractive.

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Conflict of Interest

The authors declare no conflict of interest.
Jize Liu received his B. Eng. degree in 2017 from College of Polymer Science and Engineering, Sichuan University, Chengdu, China, and M. Eng. degree in 2020 from the State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu, China. He is now a Ph.D. student in the State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu, China. His research interests include nanostructure design and environmental-friendly fabrication of stimulus-responsive materials, interdisciplinary analysis and applications.

Xinkai Li received his B. Eng. degree in 2020 from College of Polymer Science and Engineering, Sichuan University, Chengdu, China. He is currently a graduate student in Polymer Research Institute, the State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu, China. His research interests include preparation and application of photoluminescent, electromagnetic shielding, and self-healing materials.
Xin Yang received his B.Eng. in polymer materials and engineering from Sichuan University, Chengdu, China, in 2019. He is a M.D. student in the State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University. His current research focuses on the design, synthesis, characterization, and application of self-healing polymers and smart sensors.

Xinxing Zhang received his Ph.D. degree in materialogy from Polymer Research Institute of Sichuan University, Chengdu, China in 2010. He is currently a professor of State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University. His research interests focus on high-performance polymer composites, functional intelligent materials, high-value remanufacturing based on waste polymer materials, corresponding new technology and equipment, etc.