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Development of an ultra-stretchable double-network hydrogel for flexible strain sensors

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Abstract

The applications of hydrogels are restricted by their weak mechanical properties due to the inefficient dissipation of energy in their intrinsic structures. A double-network (DN) hydrogel has been developed by combining an ionically crosslinked agar network, a covalently crosslinked acrylic acid (AAC) network, and a dynamic and reversible ionically crosslinked coordination between AAC chains and Fe^{3+} ions. A model has been proposed to reveal the mechanism of the improved mechanical properties in the DN agar/AAC- Fe^{3+} hydrogel. The hydrogen-bond crosslinked double helices of agar and ionic-coordination interactions of AAC- Fe^{3+} serve as sacrificial bonds during large deformation to dissipate the energy while the reversible AAC- Fe^{3+} interactions can be regenerated after stress relief, which greatly increases the toughness of the DN hydrogel. The prepared DN hydrogel demonstrates a remarkable stretchability with a break strain up to 3174.3%, a high strain sensitivity with a gauge factor of 0.83 under the strain of 1000%, and a good 3D printability which guarantee its various potential applications in flexible strain sensors for human motion detection, electronic skin, and soft robots.

Keywords: Hydrogel, Acrylic acid, Agar, Flexible strain sensor, 3D printing

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1. Introduction

Hydrogels are usually recognized as soft and wet materials. The weak mechanical properties of hydrogels caused by the inefficient energy dissipation in their intrinsic structures of polymer networks restrict their applications in tissue engineering, sensing, and soft actuators¹. Different approaches have been developed to design mechanically robust hydrogels with specific network structures and energy dissipation mechanisms for improving their strength and toughness, such as nanocomposite hydrogels²⁻³, ionically crosslinked hydrogels⁴⁻⁶, macromolecular microsphere composite hydrogels⁷⁻⁸, and double network (DN) hydrogels⁹⁻¹⁰.

Among these tough hydrogels, DN hydrogels first developed by Gong et al. have received tremendous attention due to their remarkable mechanical performances⁹⁻¹¹. DN hydrogels consist of two networks, a tightly crosslinked brittle network and a loosely crosslinked ductile network¹⁰. The brittle network is usually sacrificed under large deformations to efficiently dissipate energy and protect the ductile network¹⁰. As both networks in the traditional DN hydrogels are chemically crosslinked, the fracture of the brittle network via the breakage of covalent bonds is irreversible, leading to permanent damages in the hydrogel structure. To address the issue, reversible bonds are introduced to form physical crosslinks in the brittle network to endow DN hydrogels with self-recovery capability. For example, Sun et al.¹ prepared Ca²⁺-alginate/polyacrylamide (PAAM) DN hydrogels by combining the ionically crosslinked alginate network and the covalently crosslinked PAAM network. The obtained DN hydrogels had a high fracture energy of ~9000 J m⁻² and a self-recovery capability (74% toughness recovery after resting for 24 hours at 80 °C). Apart from the

ionic interactions, hydrogen bonds were also introduced in the brittle network¹²⁻¹³. Chen et al.¹² developed agar/PAAM DN hydrogels, in which the brittle agar network was crosslinked by hydrogen bonds and the ductile network was crosslinked by covalent bonds. Different from alginate that can directly form ionic crosslinks with Ca^{2+} , carrageenan creates crosslinks through ionic association between its double helix and cations (e.g., K^+ , Ca^{2+} , and Zr^{4+}) by changing the temperature¹⁴⁻¹⁷. Several groups¹⁶⁻¹⁷ synthesized tough carrageenan/PAAM DN hydrogels combining an ionically crosslinked carrageenan network with a covalently crosslinked PAAM network to obtain high self-recoverability.

In addition to the introduction of physical crosslinks in the brittle network, tough and self-recoverable DN hydrogels were also developed by dual crosslinking of the ductile network¹⁸. Metal–ligand coordination is one of the dynamic macromolecular interactions widely used in the formation of hydrogel networks for its relatively large binding energy and stimuli-responsive functions¹⁹⁻²¹. Inspired by this strategy, DN hydrogels with dynamic metal interactions are developed in this study.

Flexible strain sensors are promising for diverse applications in electronic skin²²⁻²³, motion detection²⁴⁻²⁵, and soft robotics²⁶. However, the reported strain sensors have obvious limitations including poor stretchability and narrow detection range. Traditional metal-based strain sensors are flexible, but they can only sustain a strain less than 5% due to the very limited stretchability of metal^{23, 27}. Representative strain sensors using carbon nanotubes²⁸⁻²⁹, conductive polymer³⁰⁻³¹, and graphene³² as the conductive materials combined with elastomeric substrates were fabricated.

However, most of these sensors have a limited range of stretching (sustain strain less than 200%). It is still a challenge to fabricate flexible strain sensors with a high stretchability and strain sensitivity for applications in human motion detection³³. Interestingly, attributed to the movement of ions, DN hydrogels are conductive even under large strain. The merit of electrical conductivity makes DN hydrogels attractive materials for strain sensors to detect human motions. It is of our great interest to fabricate extremely stretchable strain sensors using conductive hydrogels.

Here, a DN agar/acrylic acid (AAC) hydrogel consisting of physically crosslinked agar as the brittle network and chemically crosslinked AAC as the ductile network was synthesized. The coordination interaction between carboxylic acid groups and Fe^{3+} ions in the ductile network could further improve the mechanical strength and electrical conductivity of the prepared hydrogels. The DN agar/AAC- Fe^{3+} hydrogel exhibited an ultra-stretchable property and good conductivity. The toughening mechanism, self-healing property, 3D printability, and strain sensitivity of the prepared DN agar/AAC- Fe^{3+} hydrogel were discussed.

2. Experimental section

2.1 Materials

Agar, acrylic acid (AAC), N, N'-methylenebisacrylamide (MBIS), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, photo initiator Irgacure 2959 (I2959) were purchased from Sigma-Aldrich, Singapore and used without further purification.

2.2 Hydrogel preparation

Agar and AAC with various weight ratios were mixed with a certain amount of MBIS and I2959. The total concentration of agar and AAC in the mixture was fixed at 20 wt %, the concentration of MBIS and I2959 were 0.1 wt % and 0.2 wt % based on the weight of AAC. Prescribed amounts of agar, AAC, MBIS, I2959 were mixed in deionized (DI) water and continuously stirred for 15 min at 95 °C. The obtained mixture was transferred to a petri dish and kept at 4 °C for 30 min to form a physically crosslinked agar network. After that, the mixture was exposed to UV light for 15 min at room temperature in a UV flood at a wavelength of 365 nm and an intensity of 60 mW/cm² (Shuttered UV system, Epoxy and equipment technology Pte Ltd) to produce the chemically crosslinked AAC network. Finally, the prepared DN hydrogel was incubated in an aqueous solution with a specific concentration of Fe³⁺ ions (0–0.5 wt % based on the weight of AAC in the hydrogel) for three days to form metal coordination interactions between the Fe³⁺ ions and the carboxyl groups of AAC.

2.3 Characterizations

Tensile tests were carried out using an uniaxial tensile tester (Instron 5569; U.K.) at room temperature with a 10 N load cell. Samples with an initial gauge length of 10 mm, a width of 5 mm, and a thickness of 3 mm were prepared. All the tensile tests were performed at a constant loading rate of 50 mm min⁻¹. Tensile modulus E was obtained from the slope of the linear region of the stress-strain curves from 0 to 10% strain. Breaking stress σ_b and breaking strain ε_b were estimated from the stress-strain curves obtained from at least three separate tests.

Stretch ratio λ was defined as the final length divided by the original length of the sample. In a hysteresis measurement, the samples were first stretched to a pre-set stretch ratio and then unloaded to zero strain at a speed of 50 mm min⁻¹. The dissipated energy (U_{hys}) was estimated by the area enclosed by the loading and unloading curves.

The self-healing behavior of the DN agar/AAC-Fe³⁺ hydrogel was investigated at 25 °C and 95 °C, respectively. The self-healing properties of the hydrogel was assessed by cutting the samples into several pieces and bringing the freshly cut surfaces in contact with each other without adding any chemicals. The samples were sealed in a polyethylene bag and then soaked in a water bath at 95 °C for 15 min. The healed samples were stored at room temperature for half an hour before tensile tests to verify their self-healing capability.

A 3D printer (BioFactory bioprinter machine, RegenHU) was used for printing the DN agar/AAC-Fe³⁺ hydrogel. The temperature for printing the hydrogel structure was around 20 °C which is the working temperature of this printer. The inner diameter of the nozzles used for printing was 0.25 mm (25 GA). The extrusion pressure used for printing was 0.8 bar. The DN hydrogel was partially crosslinked by exposing it to UV light for 5 min before printing. After printing, the printed 3D structures were exposed to UV light for 10 min for further structural strengthening. A hollow spiral structure and grids were printed.

A strain sensor was assembled by using the agar/AAC-Fe³⁺ hydrogel as the conductor. The elastomeric substrates were made out of a very high bond (VHB) tape that was transparent and stretchable. Two extra pieces of the VHB tape were attached on the top and bottom surfaces of the hydrogel to encapsulate the copper wires connected to the electrometer (Keithley, model 2450). Finally, the strain sensor was attached to a finger. Its resistance was monitored as it underwent varying degrees of strain due to the bending of the finger.

3. Results and discussion

3.1 Formation of the DN agar/AAC-Fe³⁺ hydrogel

The synthesis process of the DN agar/AAC-Fe³⁺ hydrogel is illustrated in **Figure 1**. The agar chains underwent the coil-helix transition followed by the aggregation of the double helices during cooling. The physically crosslinked agar network was formed as the brittle network. After UV curing, chemical crosslinks were formed in photopolymerizable AAC that served as the ductile network. The obtained DN agar/AAC hydrogel was soaked into a Fe³⁺ solution for three days at room temperature to form ionic coordination interactions between Fe³⁺ ions and carboxyl groups of the AAC chains. The carboxyl-Fe³⁺ coordination interactions could provide additional strength to the ductile network of soft AAC to withstand large stress under deformation.

Figure 1. Schematic illustration of the preparation process of the Fe³⁺ ions-reinforced DN agar/AAC-Fe³⁺ hydrogel.

3.2 Mechanical properties of the DN agar/AAC-Fe³⁺ hydrogel

Representative tensile stress-strain curves for single network (SN) agar, SN AAC and Fe³⁺ ions-reinforced agar/AAC DN hydrogels (DN agar/AAC-Fe³⁺) are shown in **Figure 2a**. The physically crosslinked SN agar hydrogel exhibited a tensile breaking strain ε_b of 27.8%, breaking stress σ_b of 8.2 kPa, and Young's modulus E of 32.3 kPa. Whereas the chemically crosslinked

SN AAC hydrogel demonstrated a much improved stretchability with ε_b of 1529.7%, σ_b of 15.7 kPa, and E of 10.1 kPa. The combination of the two SN hydrogels endowed the resultant DN agar/AAC-Fe³⁺ hydrogel with superior mechanical properties. Both ε_b (3174.3%) and σ_b (69.6 kPa) of the DN hydrogel far exceeded those of the two SN hydrogels.

Figure 2. DN agar/AAC-Fe³⁺ hydrogel showing extraordinary mechanical properties: (a) tensile stress–strain curves for the SN agar, SN AAC, and DN agar/AAC-Fe³⁺ hydrogels; photographs of the DN agar/AAC-Fe³⁺ hydrogel under (b) bending, knotting, and (c) stretching.

The ultrahigh stretchability of our proposed DN hydrogel was superior to those of the previously reported DN agar/PAAM^{12, 34}, Fe³⁺ ions-reinforced AAC³⁵, and agar/poly (N-hydroxyethyl acrylamide)-AAC-Fe³⁺ hydrogels³⁶ with a breaking strain of 2000, 1400 and 1100%, respectively. The elastic modulus (90.2 kPa) of the DN hydrogel was larger than the sum of the

elastic moduli of the two SN hydrogels. Shown in **Figure 2b and c**, the DN hydrogel could be bent, knotted, and conveniently stretched to more than 20 times of its original length even after being knotted, demonstrating its excellent mechanical properties.

Mechanical properties of the DN agar/AAC-Fe³⁺ hydrogel depended on the compositions of agar (brittle network), AAC (ductile network), and Fe³⁺ ions (formation of ionic crosslinks). Thus, the effect of the weight ratio of agar to AAC and the content of Fe³⁺ ions on the mechanical properties of the DN agar/AAC-Fe³⁺ hydrogel was investigated.

Figure 3a illustrates the effect of the weight ratio of agar to AAC on the mechanical properties of the DN agar/AAC-Fe³⁺ hydrogel. Both breaking stress σ_b and elongation at break ε_b increased with a decreasing weight ratio of agar to AAC up to 0.2/1.8, as shown in **Figure 3b and c**. A further decrease in the weight ratio of agar to AAC (e.g., 0.0/2.0) resulted in a decrease in σ_b and ε_b . Physical bonds such as ionic bonds, hydrogen bonds, and hydrophobic association are generally weaker than covalent bonds. As a result, in the DN hydrogel, the hydrogen bond crosslinked double helices were broken first under deformation and served as the sacrificial components, which may establish an efficient energy-dissipation mechanism to avoid breaking the main framework of the hydrogel and enhance the toughness of the integral structure. Due to the proposed energy dissipation mechanism in the DN hydrogel, the toughness was larger than that of the hydrogen bond crosslinked SN agar hydrogel and chemically crosslinked SN ACC hydrogel with the weight ratio of agar to AAC being 0.0/2.0. Therefore, this weight ratio was fixed at 0.2/1.8 for subsequent studies.

Figure 3. The effect of the weight ratio of agar to AAC on the mechanical properties of the DN agar/AAC-Fe³⁺ hydrogel with the content of Fe³⁺ ions fixed at 0.2 wt % of AAC: (a) tensile stress–strain curves, (b) maximum tensile strength, and (c) elongation at break. The effect of the content of Fe³⁺ ions on the mechanical properties of the DN agar/AAC-Fe³⁺ hydrogel with the weight ratio of agar to AAC fixed at 0.2/1.8: (d) tensile stress–strain curves, (e) maximum tensile strength, and (f) elongation at break. The concentration of MBIS and I2959 were fixed at 0.1 and 0.17 wt % of AAC, respectively.

The effect of the content of Fe³⁺ ions on the mechanical properties of the DN agar/AAC-Fe³⁺ hydrogels was investigated. As shown in **Figure 3d**, the prepared agar/AAC hydrogel without the

reinforcement of Fe^{3+} ions (a Fe^{3+} content of 0.0 wt%) shows poor mechanical properties with ε_b of 1708.3%, σ_b of 40.2 kPa, and E of 27.06 kPa. After the introduction of 0.2 wt % of Fe^{3+} ions in the agar/AAC hydrogel, the obtained DN agar/AAC- Fe^{3+} hydrogel demonstrated much enhanced mechanical properties (ε_b of 3174.3%, σ_b of 69.6 kPa, and E of 90.2 kPa). The results indicated that the mechanical properties of the agar/AAC hydrogels could be significantly improved by the further creation of coordination interactions between the carboxylic acid groups of AAC and Fe^{3+} ions. The strong and flexible DN agar/AAC- Fe^{3+} hydrogel could sustain various forms of deformations as shown in **Figure 2b and c**.

Upon increasing the content of Fe^{3+} from 0 to 0.2 wt %, σ_b slightly increased from 40.2 kPa to 69.1 kPa while ε_b sharply increased from 1708.3% to 3174.3%. DN agar/AAC- Fe^{3+} with higher Fe^{3+} contents (0.3 and 0.5 wt %) could sustain a higher tensile stress but showed a weaker stretchability. As the aim of this work was developing ultra-stretchable hydrogels, the Fe^{3+} content was fixed at 0.2 wt % for subsequent studies.

The microstructures of the SN agar, SN AAC, and DN agar/AAC- Fe^{3+} hydrogels are shown in **Figure S1**. The average pore sizes of the SN agar, SN AAC, and DN agar/AAC- Fe^{3+} hydrogels were 213.8, 37.6, and 20.6 μm , respectively. The SN agar hydrogel displayed a uniform porous structure. The SN AAC hydrogel showed a porous structure with smaller pore sizes than SN agar. The pore size of DN agar/AAC- Fe^{3+} was smaller than those of SN agar and SN AAC, revealing an increased crosslinking density and a compact hydrogel matrix. Moreover, the pores in DN agar/AAC- Fe^{3+} had very similar sizes and shapes.

3.3 Energy dissipation of the DN agar/AAC-Fe³⁺ hydrogel

The fracture process and toughening mechanism of DN hydrogels are complicated. Gong et al. proposed that the high toughness of chemically crosslinked DN hydrogels, such as poly (2-acrylamido-2-methylpropanesulfonic acid)/polyacrylamide (PAMPS/PAAM) DN hydrogels, could be attributed to the internal fracture of the chemically crosslinked brittle PAMPS network efficiently dissipating energy during deformation³⁷. For physically and chemically crosslinked DN hydrogels such as agar/PAAM, the toughening mechanism could be attributed to the continuous fracture of the physically crosslinked agar network¹².

Loading–unloading tensile tests at different stretch ratios were conducted to investigate the toughening mechanism of our prepared DN agar/AAC-Fe³⁺ hydrogel. The internal fracture process of the DN agar/AAC-Fe³⁺ hydrogel was discussed by assessing the capability of energy dissipation. **Figure 4a** shows the loading–unloading curves for the DN agar/AAC-Fe³⁺ hydrogel with varying stretch ratios, and their large hysteresis loops were observed. The area enclosed by the loading–unloading curves is defined as the dissipated energy of one cycle. The expanded hysteresis loops with the increasing stretch ratio indicated a gradual internal fracture process of the DN hydrogel. When the DN agar/AAC-Fe³⁺ hydrogel was stretched to a small ratio, the double-helical aggregates in the physically crosslinked agar network started to be unzipped. The double-helical aggregates were unzipped progressively upon increasing the stretch ratio while the chemically crosslinked AAC network remained intact to stabilize the overall structure of the DN hydrogel. Meanwhile, the dynamic and reversible ionic coordination interactions between AAC and Fe³⁺ enabled the unfolding and refolding of the AAC chains during stretching. Moreover, physical bonds including hydrogen bond, ionic bond, and hydrophobic association are generally weaker than covalent bonds. These weak bonds could be sacrificed during large deformation, thus establishing an efficient energy dissipation mechanism to avoid permanent damages in the main framework and increase the toughness of a material. In the prepared DN hydrogels exhibiting pronounced hysteresis, the

weak bonds including the hydrogen bond crosslinked double helices and ionically crosslinked metal coordination were broken first to dissipate energy under large deformation, while the strong bonds were retained to resist further deformation. When the stretch ratio λ increased from 6 to 21, U_{hys} increased significantly from 129.31 to 628.93 kJ m⁻³ (**Figure 4b**), indicating that the prepared DN hydrogel can effectively dissipate energy at large deformation.

Figure 4. Mechanical performance of the DN agar/AAC-Fe³⁺ hydrogel under different stretch ratios: (a) tensile loading–unloading curves and (b) corresponding dissipated energy of the hydrogel under varying stretch ratios.

3.4 Self-healing experiment

Self-healing is the capability of a material to recover from physical damage^{38–40}. The self-healing behavior of DN agar/AAC-Fe³⁺ hydrogel was investigated at 25 °C and 95 °C. As shown in **Figure 5a**, the freshly cut DN agar/AAC-Fe³⁺ hydrogel pieces were brought into contact with each other to form a string at 25 °C. The string of hydrogel pieces could stand up and be lifted immediately after the contact, indicating the self-healing behavior of the DN agar/AAC-Fe³⁺ hydrogel pieces in contact with each other at room temperature. This behavior was due to the formation of coordination interaction between the Fe³⁺ ions and carboxyl groups of AAC at 25 °C, as shown in **Figure 5d**.

Figure 5. Photograph and schematic demonstration of the self-healing performance of the DN agar/AAC-Fe³⁺ hydrogel at 25 °C and 95 °C. (a) Freshly cut hydrogel pieces were attached together into a string at 25 °C. The self-healed sample could stand vertically or be lifted up to withstand the weight. (b) Two freshly cut hydrogels pieces were put into contact with each other and healed at 95 °C for 15 min. The healed sample could be stretched after healing. (c) Stress-strain curves of the self-healed and original samples. The self-healed sample could sustain the stretching to about 1.5 times of its original length. (d) Schematic illustration of the self-healing process between two hydrogels pieces at 25 °C and 95 °C.

It is well-known that the sol-gel and gel-sol transitions of agar in aqueous solution are thermoreversible⁴¹⁻⁴². Due to the thermoresponsive property of agar, the cut surfaces of the DN agar/AAC-Fe³⁺ hydrogel could be reconnected and self-healed at an elevated temperature. More specifically, the double helices of agar could be transformed into coils under heating and

reassociated to form double helices after cooling. The self-healing property can be observed by annealing the cut samples at 95 °C for 15 min. As shown in **Figure 5b**, the two freshly cut pieces were well-healed and integrated into one part that can be stretched. However, the mechanical property of the healed sample was weaker than that of the original sample according to their stress-strain curves. The self-healed sample could be only stretched to about 1.5 times of its original length (**Figure 5c**). It was because that the self-healing process mainly took place in the physically crosslinked agar network through the coil-helix transition and reassociation of double helices, as demonstrated in **Figure 5d**. In the AAC network, only the coordination interactions between the Fe^{3+} ions and carboxyl groups of AAC could be regenerated with the broken chemically crosslinked portion. Hence, the healing efficiency of DN agar/AAC- Fe^{3+} hydrogels was not as high as expected.

3.5 3D printing of hydrogel structures

The 3D printing of soft polymer materials is still challenging⁴³⁻⁴⁶, although some of them have excellent mechanical properties. The poor printability of the DN hydrogel without UV curing could be addressed by exposing the hydrogel to UV light for 5 min for partial crosslinking before printing (Supporting Information, **Figure S2**). A 15-layer hollow spiral structure and a 50-layer grid structure were printed, as shown in **Figure 6**. Structures with complex geometry including the delicate internal porous geometry could be printed. Additionally, the shape of the printed 3D structures highly matched the pre-designed pattern, indicating a good printability of the DN agar/AAC- Fe^{3+} hydrogel. The width of each printed filament conformed to the diameter of the nozzle used (0.25 mm).

Figure 6. Images of 3D printed structures: a hollow spiral structure with 15 layers (height is about 3.5 mm) and a grid structure with 30 layers (height is about 7.2 mm).

3.6 DN agar/AAC- Fe^{3+} hydrogel-based strain sensor

Illustrated by **Figure 7a**, a complete circuit comprising a light-emitting diode (LED) indicator was used for illustration the conductivity of the DN agar/AAC- Fe^{3+} hydrogel. The LED indicator lighted up when a voltage of 3 V was applied. After the hydrogel sample was cut into two pieces, the LED indicator was deactivated. The cut hydrogel pieces were healed by putting the freshly cut surfaces back into contact at 95 °C for 15 min. The healed hydrogel worked as a conductor again indicated by the emitted light of the LED indicator. The self-healing property of the soft strain sensors that can recover mechanical performance even at the damaged region or extremely stretched region is significant to avoid the sensor degradation or failure under deformation.

Hydrogels containing a large amount of water did not only show physical similarity to bio-tissues, but also present the capability of containing lots of mobile ions.⁴⁷⁻⁴⁸ The DN agar/AAC- Fe^{3+} hydrogel possessed ionic conductivity due to the presence of Fe^{3+} ions in the network. To investigate the electrical sensitivity of the DN agar/AAC- Fe^{3+} hydrogel, its resistance and corresponding gauge factors under different tensile strains were measured. The gauge factor is

defined as the ratio of relative resistance change $(R - R_0)/R_0$ to the applied strain ε , where R and R_0 are the resistance with and without the applied strain, respectively. As shown in **Figure 7b**, the gauge factor was 0.46 under a strain of 100% and increased to 0.83 as the strain increased to 1000%, indicating a high strain sensitivity. Conventional metal-based strain sensors have a gauge factor of 2.0, but they show a poor stretchability (sustainable strain less than 5%)^{23, 27, 23, 49}. Yao et al.⁵⁰ developed a stretchable sensor using silver nanowire, which could detect tensile strain up to 50% with a gauge factor of 0.7. Yamada developed a stretchable electronic strain sensor for human-motion detection, which could achieve a wide strain detection range of ~60–200% with a small gauge factor of 0.06²⁹. The trade-off between stretchability and electrical sensitivity of stretchable electrical materials caused difficulties in producing high-performance strain sensors. Although the gauge factor of our DN agar/AAC-Fe³⁺ hydrogel is lower than that of conventional metal-based strain sensors, it is still higher than that of the hydrogel-based sensors (a gauge factor of 0.23 at a strain of 100%)³³, piezoresistive electronic strain sensors (a gauge factor of 0.06 at a strain of 200%)²⁹, and capacitive soft strain sensors (a gauge factor of 0.348 at a strain of 700%)⁵¹. Our developed DN agar/AAC-Fe³⁺ hydrogel integrated the attributes of stretchability and electrical sensitivity to fabricate high-quality stretchable strain sensors.

Owing to the high electrical sensitivity and excellent stretchability, the performance of the DN agar/AAC-Fe³⁺ hydrogel as a stretchable electronic device was further evaluated. In **Figure 7c**, the assembled DN agar/AAC-Fe³⁺ hydrogel-based strain sensor was attached to a finger to detect the bending and stretching motions of the finger. The resistance of the strain sensor increased to different levels when increasing the bending degree of the finger, as shown in **Figure 7d**. The results indicated that the assembled strain sensor was capable of distinguishing the different bending angles of the finger. More importantly, the resistance of this sensor could immediately fall back to the initial level after the finger was relaxed. The developed DN hydrogel is sensitive to human motions and is an ideal candidate for fabricating stretchable electronic devices.

Figure 7. Electrical properties of the DN agar/AAC- Fe^{3+} hydrogel: (a) a circuit with an LED indicator for demonstrating the conductivity of the original, cut, and self-healed DN agar/AAC- Fe^{3+} hydrogels; (b) effect of various tensile strains on the gauge factor; (c) DN agar/AAC- Fe^{3+} hydrogel-based strain sensor mounted onto an index finger that bent at different degrees; (d) real-time record of the resistance of the hydrogel under different finger motions.

4. Conclusions

A highly stretchable DN agar/AAC-Fe³⁺ hydrogel with self-healing, 3D-printable, and strain sensitive properties was synthesized by combining an ionically crosslinked agar network with a covalently crosslinked AAC network and creating coordination interactions between the carboxylic acid group and Fe³⁺ ions in the AAC network.

Under deformation, hydrogen bond crosslinked double helices in agar and ionic coordination interactions in AAC-Fe³⁺ were broken first to serve as the sacrificial bonds. The behavior established an energy dissipation mechanism to avoid breaking the main framework of the DN hydrogel, resulting in the great toughness of the overall structure. The reversible ionic coordination interactions enabled the unfolding and refolding of the AAC chains. A remarkable stretchability of the DN hydrogel with the break elongation up to 3174.3% was thus achieved.

The developed DN agar/AAC-Fe³⁺ hydrogel exhibited a higher gauge factor (from 0.46 at a strain of 100% to 0.83 at a strain of 1000%) than most of the previously reported strain sensors. The DN hydrogel integrated the attributes of stretchability and strain sensitivity to realize the fabrication of stretchable strain sensors for human motion detection. Because of the thermoreversible sol-gel transitions of agar, the DN hydrogel exhibited the self-healing property that the cut surfaces could be rebounded and healed via a gel-sol-gel transition in a heating-cooling cycle. In addition, the DN hydrogels presented 3D printability through being used as inks for the printing of complex structures. This work is the first to demonstrate not only ultra-stretchable and self-healing properties but also high 3D printability and strain sensitivity of the DN hydrogel.

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