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Template method for dual network self-healing hydrogel with conductive property

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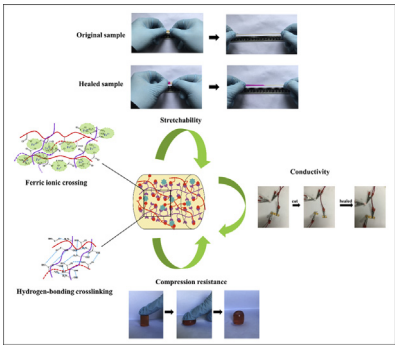
HIGHLIGHTS

- Chitosan-based self-healing hydrogels with dual-network crosslinks (hydrogen bonds and ionic linkage) were fabricated.
- The self-healing efficiency and compression deformation could attain 93.8% and 98.5%, respectively.
- Iron ions contributed to the self-healing property, compression resistance, and conductivity of the as-prepared hydrogels.

GRAPHICAL ABSTRACT



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ABSTRACT

We herein present dual-network self-healing hydrogels via ionic cross-linking and hydrogel bonds based on chitosan molecular chain as a template. Chitosan and poly(acrylic acid) were reacted to form a dual-network structure via Fe^{3+} ion coordination and hydrogen bonds. The healing property mainly depends on the coordination between Fe^{3+} ions and —COOH or —NH_2 groups of the polymer chains, as well as on the hydrogen bonds occurring among —OH, —NH_2 and —COOH groups. Compared with the covalent cross-linking points, the ionic linkages and hydrogen bonds in the hydrogels were stochastic and dynamic. Hence, if the hydrogel becomes cracked or possesses a notch, the cross-linking points will be destroyed, while the new ones will be re-formed based on the dual-network of the hydrogel. The self-healing efficiency of the as-prepared hydrogel could reach 98.5% when the concentration range of 0.01–0.5 M Fe^{3+} aqueous solution was used. In addition, both the compression resistance and electrical conductivity of the hydrogel were enhanced with $FeCl_3$ content increasing. Therefore, the as-prepared hydrogel exhibited excellent stretchability, compression resistance, self-healing performance without any external stimulus, and electrical conductivity.

1. Introduction

Generally, the human skin, muscles, and ligaments exhibit self-repairing properties based on capsule, vascular, and intrinsic system effects. Inspired by biological systems in which damage triggers an autonomic healing response, self-healing materials, which can repair damage when cracked, prolong their lifetime, and save costs, have gained increasing popularity [1–3]. Hence, self-healing materials have been attempted to be used in the fields of medical, heavy ions detection, catalyst [4,5], supercapacitor [6,7], drug delivery [8], and coating [9], just to mention a few.

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Among self-healing materials, self-healing hydrogels exhibit a promising material as hydrogel is one of the most promising candidates in multiple bio-applications including drug delivery, tissue engineering [10,11], and cell proliferation temporary substrate [12]. Based on the cross-linking points, hydrogels can be divided into physical hydrogels which include cross-linking hydrogels with hydrogen bonding [13,14], electrostatic ionic force [15], π-π stacking [16], hydrophobic interaction, and host-guest inclusion [17], and chemical hydrogels which include dynamic covalent bonds, such as Schiff base linkages [18], acylhydrazone bonds [19,20], disulfide bonds [21], boron ester bonds (reaction of boronic acid with diol) [22], and non-dynamic covalent bonds that cannot be re-formed after breakage. However, of all the previously mentioned, the hydrogel with the dynamic cross-linking points, which contain either physical or dynamic covalent bonds, is more beneficial to healing after being destroyed or cut [23–25]. For example, Pan et al. [26] constructed polymer/graphene oxide (GO) nanocomposite hydrogels which achieved self-healing property based on ionic bonds between 2-(dimethylamino)ethylacrylatemethochloride and GO and the hydrogen bonds between acrylamide and GO. While Kang et al. [27] fabricated a supramolecular polymer film with water-insensitive self-healing ability via a mixture of strong and weak crosslinking hydrogen bonds. Furthermore, Nevejans et al. [28] elucidated self-healing property of poly(disulfide)s based on disulfide bonds.

Chitosan has received significant attention in biomedical sciences because of its mucoadhesity, low cytotoxicity, biodegradability, antibacterial ability, and hemostatic ability [29–31]. Given that chitosan is derived from chitin by removing the acetyl groups, the hydrophilicity and appropriate amount of amine groups of chitosan depend on deacetylation degree [32]. Moreover, the amine and hydroxyl groups in the chitosan skeleton can be used for further functionalization [33], and formation of hydrogen bonds intramolecularly, intermolecularly and with groups such as —NH_2, —COOH, and —OH from other molecules. In addition, the amino groups of chitosan can also be protonated in acid aqueous solution and form composites with negatively charged molecules or materials [34], and can even form chelates with metal ions [35]. These properties make chitosan an ideal candidate for self-healing hydrogel material. For instants, Ren et al. [36] fabricated self-healing film using chitosan (CS) and dialdehyde functioned poly (ethylene glycol) (DF-PEG). Li et al [37] fabricated injectable chitosan-based self-healing hydrogel for bioapplications. However, the chitosan-based hydrogels are soft and stretchable but with poor compressive capacity. So methods were explored to enhance the tough of the hydrogel based on chitosan. For example, Azevedo et al. [38] functionalized chitosan with catechol groups to form coordination bonds with Fe^{3+} ions and a chemical crosslinker was used to obtain the toughened self-healing hydrogel. Li et al. [39] also fabricated tough self-healing hydrogel as nano-fibrous aggregates of chitosan were formed in the hydrogel. Despite all these reported works, there is yet any literature report that uses physical cross-linking bonds to enhance the compression of chitosan-based self-healing hydrogel.

In this study, we report a method to fabricate self-healing hydrogels based on chitosan instead of synthesizing complex macromolecules with multi-steps under mild conditions. Generally, researching autonomous self-healing materials without external stimuli is still a challenging issue under ambient conditions. Herein, a template-based one-pot method for fabricating self-healing hydrogel is shown in Fig. 1. First, chitosan was dissolved in 1% (vol%) glacial acetic acid aqueous solution, and then acrylic acid (AA) and ferric ions (Fe(III)) were added. Herein, the chitosan molecule plays the role of a template, with AA molecules combining to the chitosan skeleton via hydroxyl bonds, while Fe(III) coordinates with –COOH of AA and -NH_2 of chitosan. After carrying out homogeneous mixing, potassium sulfite (KPS) was used as an initiator to polymerize AA and form poly(AA) (PAA) through free radical polymerization. Thereafter, the double cross-linking hydrogel (labelled as CS-PAA-Fe(III)) was obtained where the first kinds of cross-linking involve intra-chain hydrogen bonding intra- or interchains of PAA and chitosan, as well as inter-chain hydrogen bonding between PAA and chitosan, while the second cross-linking is the coordination of Fe^{3+} with –COOH of PAA or -NH_2 of chitosan, or both. To observe the self-healing property of CS-PAA-Fe(III), the hydrogel was cut with a blade, and the freshly-cut section of the hydrogel re-contacted and healed without external stimulus.

2. Materials and methods

2.1. Materials

All reagents were of analytical grade and used without further purification. Chitosan,(MW 400–2000 kDa, deacetylation degree > 95%) was purified by reprecipitation from the filtered 1% acetic acid solution with ammonium hydroxide. The precipitate was washed with water and dried under vacuum. The purified chitosan was thereafter dissolved in

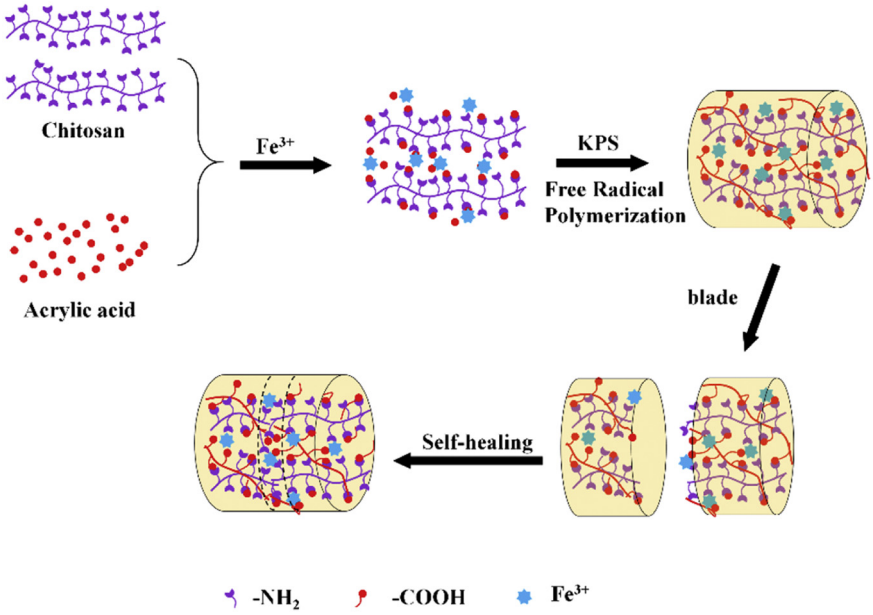

Fig. 1. Schematic description of the preparation of self-healing CS-PAA-Fe(III) hydrogels.