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Self-healing and photoluminescent carboxymethyl cellulose-based hydrogels

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ABSTRACT

Nature resource-derived hydrogels with the properties of both self-healing and photoluminescence are urgent needed to develop. Herein, we demonstrate that carboxymethyl cellulose (CMC)-based hydrogels can be engineered to exhibit the integrate capabilities of self-healing, photoluminescence and stretchability by a facile, green and economic approach. The CMC-based hydrogels present blue-green color under ultraviolet light, and self-heal in ambient temperature without any external stimulus with 95% healing efficiency. Moreover, the healed hydrogel can be stretched nearly 2.5 times of their original length. The stretchable self-healing and photoluminescent CMC-based hydrogels can adhere to glass, plastic and soft tissues. The vessel sealant for preventing the leakage of aqueous solution and prototype of mucoadhesive for stomach perforations are demonstrated. With these novel properties, the easy-to-synthesize, mass production, multifunctional smart CMC-based hydrogels hold great potential for applications in biomedical and engineering fields.

1. Introduction

Soft smart materials, sensing diversification in environment, or even perceiving and adapting the changes in their properties and functions, are increasingly being explored. Self-healing hydrogels have emerged as novel smart soft materials which can recover their desirable properties and functionalities after damage [1–5]. Recent progresses in self-healing hydrogels show their potential applications as structural materials in the fields of biomedicine (*e.g.* tissue adhesive [6], anti-biofouling substance [7] and wound dressing [8]) and engineering (*e.g.* coatings [9] and sealants [6]). Besides the excellent performances of self-healing hydrogels, there are still some challenges for their further practical applications, for example, difficulty in monitoring and detecting their performances in the process of practical applications, due to the lack of capability for monitor and tracking. On the other hand, photoluminescent hydrogels constituted by photoluminescent emitter (*e.g.* quantum dots [10], carbon dots [11] and lanthanide ions [12]) and polymer networks have been developed for widespread applications in biomedicine (*e.g.* bioimaging [13], biosensors [14], thermosensors [15]) and engineering (e.g. optical switches [16], pH sensors [10]), whereas, few of them possess self-healing capability. In response, the concept of self-healing and photoluminescent hydrogel has been proposed. Unfortunately, the development of hydrogels with

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integrated capabilities of self-healing and photoluminescence is rarely realized.

It is great challenge to explore facile approaches to achieve the self-healing hydrogels integrated with photoluminescent performance. Generally, the self-healing capability of hydrogels can be achieved by the introduction of suitable non-covalent interactions (*e.g.* hydrogen bonding [17–19], hydrophobic interaction [20,21], coordination interaction [22,23], electrostatic interaction [24,25], and host-guest interaction [26–28]) or dynamic covalent interactions (*e.g.* phenylboronate complexation [29–32] imine bond [33–35], acylhydrazone bond [36–39] and disulfide bond [9,40]) into the polymer networks of hydrogles. On the other hand, the photoluminescent capability of hydrogels can be realized via immobilization of photoluminescent emitters to polymer networks. Currently, self-healable photoluminescent hydrogels based on supramolecules have been reported. For examples, Wan and co-authors fabricated the micelle networks constructed by photoluminescent polyoxometalates ($Na_9EuW_{10}O_{36}$) and triblock polyelectrolyte, poly (2-(2-guanidinoethoxy) ethylmethacrylate)-*b*-poly (ethyleneoxide)-*b*-poly (2-(2-guanidinoethoxy)-ethylmethacrylate) (PG_n-*b*-PEO_{230}-*b*-PG_n) [41]. The micelle networks driven by electrostatic interactions among PG_n-*b*-PEO_{230}-*b*-PG_n and $Na_9EuW_{10}O_{36}$ afford self-healing capability to the supramolecular hydrogel. Tian et al. synthesized a self-healing hydrogel with photostimulated room-temperature phosphorescence responsiveness [42]. The host-guest recognition of poly(*β*-cyclodextrin) and poly(α-bromonaphthalene) simultaneously endues the capabilities of self-healing and phosphorescence to the supermolecular hydrogel. These designs inspire us to fabricate the hydrogels possessing the capability of self-healing and photoluminescence via integrating various ingredients with desired properties. Moreover, mass production and economic practicality are desired for the multi-functional hydrogels as structural materials in the fields of biomedicine and engineering. Thus, it is expected to develop promising self-healing and photoluminescent hydorgels through facile strategy using green, cheap and natural resources. However, it is still elusive to explore the hydrogels with the multifunction of self-healing and photoluminescence using nature green resources.

Carboxymethyl cellulose (CMC), a cellulose derivative hangling carboxymethyl groups ($-CH_2COO^-$) on the cellulose backbone, is one of the most abundant nature-derived green and renewable resources with the virtues of biocompatibility, biodegradability, low-cost and large storage. CMC-based hydrogels have been broadly utilized in the areas of tissue engineering [43,44], drug/cell delivery [45,46], wound dressing [46], wastewater treatment [47] and plant breeding [46,48]. Self-healing CMC hydrogels based on hydrogen bondings [49] and dynamic phenylboronate ester crosslinks [50] have been reported. It is still struggle to develop the self-healing CMC-based hydrogels integrated with the properties of photoluminescence.

In this contribution, we propose that the capabilities of autonomic self-healing and photoluminescence could be achieved in CMC-based hydrogels by doping appropriate amount of aluminum (Al^{3+}) ions and photoluminescent citric acid derivatives (PCAD) into CMC polymer networks. The self-healing capability is derived from the reversible ionic coordination between Al^{3+} ions and carboxylate groups ($-COO^-$) dangling both on PCAD and CMC polymer chains.

The PCAD serve the following two functions in the hydrogels. (i) As photoluminescent emitter which endowing photoluminescent capability to the hydrogels; (ii) The $-COO^-$ groups of PCAD (PCAD-COO^-) appropriately attenuate the strong ionic interaction between Al^{3+} ions and the $-COO^-$ groups hanging on CMC polymers (CMC-COO^-), which facilitating dynamic ionic coordination interactions for achieving self-healing capability to the hydrogels. The CMC-based hydrogels presented blue-green photoluminescence can self-healing in ambient temperature without any external stimulus, and the healing efficiency of tensile stress can reach up to 90%. As prototypes of applications of the CMC-based self-healing and photoluminescent hydrogel, we further demonstrated the sealants for vessels containing aqueous solution and mucoadhesive for stomach perforations. The novel facile and mass productive strategy of achieving the hydrogels integrated with self-healing and photoluminescent capabilities can be adapted for other natural polymers which broadening multifunctional hydrogel frontiers.

2. Materials and methods

2.1. Materials

Sodium carboxymethyl cellulose (CMC, 1500–3100 mPa·s, Mw = 250,000 Da) and anhydrous citric acid (AR) were purchased from Aladdin Chemistry. N,N′-Carbonyldiimidazole (CDI, AR) was obtained from Shanghai Medpep. Aluminum chloride hexahydrate ($AlCl_3$ $6H_2O$, AR) was form Sinopharm Medicine. Methylene blue, phenol red and rhodamine B (95%) were supplied by Sigma-Aldrich. All other chemicals are analytical grade and used without further purification.

2.2. Preparation of PCAD and CMC-based hydrogels

The blue-green photoluminescent PCAD can be obtained through grinding fine powder of citric acid and CDI (molar ratio of citric acid to CDI is 1:1.2) into a mortar at room temperature. After grinding for several minutes, the white powder mixture became sticky and the color gradually changes from yellow to dark brown. Accompanying the reaction, the products begin to display blue-green photoluminescent under UV irradiation (365 nm), and the photoluminescent intensity gradually increases with reaction time. The absorption and emission peak of the aqueous solution of PCAD is 381 nm and 483 nm, respectively. The chemical structure of citric acid and PCAD was characterized by ^1H NMR (Bruker-400 MHZ, German Bruker Co, 400 MHz).

2.3. Fourier transformed infrared spectroscopy (FTIR)

The CMC-based hydrogels were fabricated by a facilely two-step method. In the first step, a semitransparent paste-like suspension comprises of 6 wt% CMC was prepared in the mold with desired shape. The second step is a gelation process. The mixture aqueous