

Mechanically redox-tunable hydrogels reinforced by hydrophobic association and metal ion coordination

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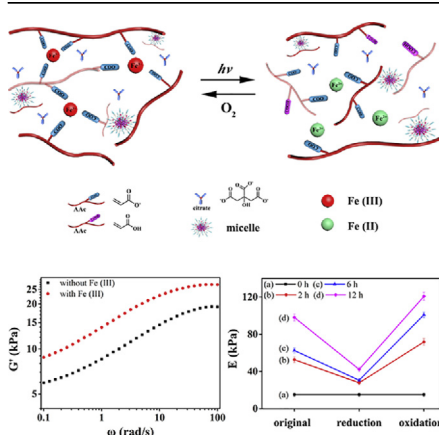
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HIGHLIGHTS

- A novel strategy for designing and preparing a mechanically redox-tunable hydrogel.
- Enhancing the mechanical strength of hydrogels by hydrophobic association effects.
- Adjusting the mechanical property of hydrogels by valent transformation between ferrous and ferric ions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Available online 28 December 2017

Keywords:

Hydrogels
Stimuli-responsive
Tunable mechanical property
Hydrophobic association
Redox

ABSTRACT

Generally understanding of stimuli-responsive hydrogels is sol-gel transition under various stimulus. However, current knowledge from stimuli-responsive hydrogels always meets poor mechanical property with a gel state. Although the proposed method of hydrophobic effect usually introduced into hydrogels to design various types of tough hydrogel, the mechanically tunable hydrogel by stimulus response was rarely reported. Herein, a mechanically redox-tunable hydrogel driven by valent transformation between ferrous and ferric ions was designed and prepared. The mechanical strength of hydrophobic association hydrogels can be easily reduced by destroying metal complexation, due to the transformation from ferric to ferrous ions assisted by ultraviolet-sensitive citric acid molecules. Moreover, the mechanical strength of reduced hydrogels can be significantly enhanced through the reforming interaction between ferric ions and carboxylate groups of hydrogels exposed to oxygen. It is envisioned that the mechanically stimuli-tunable strategy would provide new insights for designing the novel stimuli-responsive hydrogels.

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1. Introduction

Hydrogels owned distinctive attributes including high water contents, permeable to various chemical and biological molecules,

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biocompatible and had been potentially applied in regenerative medicine [1–5], shape memory devices [6], sensors [7], and other fields [8]. The mechanical property was one of the most important factors for hydrogels in many applications. Jeon et al. used a novel crosslinker that consists of an acrylic head, a hydrophobic alkyl spacer connected by carbamate, and a 2-ureido-4-pyrimidone (UPy) tail to provide both hydrophobic association and hydrogen bonds [9]. Zhang et al. prepared dual physical cross-linking hydrogels via micellar copolymerization of acrylic acid and stearyl methacrylate in an aqueous ferric chloride solution with two different types of surfactant, cetyltrimethylammonium bromide and sodium dodecyl benzene sulfonate. The introduction of hydrophobic association and ionic crosslinking between the Fe^{3+} and acrylic acid endowed the hydrogels with excellent strength and self-healing properties [10]. The physically hydrophobic association interaction was usually introduced into the hydrogels to improve the mechanical strength. The hydrophobic alkyl segments could be assembled into micelles in the presence of surfactants due to the hydrophobic effects, dissipating a large amount of energy under stretching and enhancing the mechanical strength of hydrogels [11].

Moreover, the stimuli-sensitive hydrogels attracted particular interest based on specific non-covalent and dynamic binding motifs, which could be addressed by external stimuli and easily tuned by modifying the architecture and crosslinking density. Some papers had reported the physical state transformation of the sensitive hydrogel, such as a sol-gel transition, in response to environmental stimuli including host and guest [12], pH [13], redox [14], temperature [15], light [16], and multiple external stimuli [17,18]. However, for hydrogels with a gel state, the general methods to adjust the mechanical strength of hydrogels would vary some appropriate compositions and initiators [19,20]. Rare publications have reported the adjustable mechanical property by the external stimuli-responsive conditions. For example, Meyer et al. had reported a stimuli-responsive hydrogels crosslinked by copper ions with high mechanical properties due to chemical and electrochemical manipulation [21]. Marzal et al. had reported the electroplastic elastomer hydrogels which possessed manipulating mechanical properties by electricity [22]. The mechanical properties of both hydrogels were in response to the electrochemical-sensitive condition.

Moreover, Tong et al. had reported the redox-responsive sol-gel transition for poly (acrylic acid) in an aqueous solution containing Fe(III) ions in response to light [14]. The complexation between Fe(III) ions and carboxylate groups could be destroyed under UV light due to the existence of ultraviolet-sensitive citric acid molecules. Inspired by the above strategy, herein, we prepared a mechanically redox-tunable hydrogel reinforced by hydrophobic association and metal ion coordination. Different from the electrochemical-sensitivity, it was expected that the Fe(III) ions in the hydrogel would be reduced to the Fe(II) ions under UV light in the presence of ultraviolet-sensitive citric acid molecules. Moreover, Fe(II) ions would be oxidized to Fe(III) ions by exposing to oxygen. The storage modulus (G') from rheological experiments were carried out to detect the complexation between the Fe(III) ions and the carboxylate groups of poly (acrylic acid) (PAAc). Furthermore, the uniaxial elongation measurement was conducted to measure the mechanical property. It was envisioned that the mechanically stimuli-tunable strategy would provide new insights for designing the novel stimuli-responsive hydrogels in the various applications.

2. Experimental

2.1. Materials

Acrylic acid (AAc, >98%), sodium dodecyl sulfate (SDS, >97%),

potassium persulfate (KPS, 99.5%) and iron chloride hexahydrate (Fe(III) , >99%) were supplied by Aladdin (Shanghai, China). Sodium chloride (NaCl , >99.5%) and sodium hydroxide (NaOH , >96.0%) were supplied by Beijing Chemical Reagents Factory. Hexadecyl methacrylate (HMA, 95%) was supplied by Zhejiang Kangde New Materials Co. Ltd. China. Citric acid monohydrate (>99.5%) was supplied by Tianjin Guangfu Technology development Co. Ltd. Deionized water (18.2 M Ω cm resistivity at 25 °C) was used in the experiment. All materials were used as received.

2.2. Preparation of poly(acrylic acid) hydrogels

The AAc (2 mL) with deionized water (10 mL) were added into the vial to stir until the solution became clear. Then the solution was putting in oven at 70 °C to obtain the poly (acrylic acid) (PAAc) hydrogel.

2.3. Preparation of hydrophobic association PAAc hydrogels

The hydrophobic association PAAc (PAAc/HMA) hydrogel was prepared by radical copolymerization. AAc reacted with HMA, KPS as initiation, in the presence of NaCl and SDS. Firstly, the NaCl (0.32 g) and SDS (0.8 g) were added into deionized water (10 mL) until it became clear. Next, HMA (0.3 mL) was poured into the solution until a clear solution was obtained. Then, AAc (2 mL) and KPS (0.01 g) were introduced into the above solution. All above processes had been carried out under stirring all the time at ambient temperature. Finally, the above mixture solution was carried out in oven at 70 °C till the PAAc/HMA hydrogel was obtained.

2.4. Preparation of Fe(III) -citrate complexation solution

The molar ratio of the iron chloride hexahydrate (Fe(III)) to citric acid monohydrate was fixed at 1:2 and 1:5, respectively. And the concentration of Fe(III) was 0.05, 0.3 and 0.5 mol/L, respectively. The details for preparation of Fe(III) -citrate complexation solution were given as follows. First, the citric acid monohydrate was added into deionized water until the solutions were clear under stirring. Next, the relative Fe(III) was added into the above solution to form complexation with citrate. Finally, the NaOH (10 mol/L) was added into the above solution to adjust the pH value up to 4.0 using pH Meter (METTLER TOLEDO (FE20), Shanghai). Consequently, the expected Fe(III) -citrate complexation solution was obtained.

2.5. Preparation of PAAc/HMA/ Fe(III) hydrogels

The PAAc/HMA hydrogel was immersed in Fe(III) -citrate complexation solution for 2, 6 and 12 h respectively to obtain the different PAAc/HMA/ Fe(III) hydrogels. And then the obtained PAAc/HMA/ Fe(III) hydrogel was treated with irradiation under UV light (INTELLI-RAY 600) of 315–400 nm at 40% intensity and the 175 mW/cm² peak irradiance. The reduced hydrogel was obtained. Moreover, the reduced hydrogel was put into the empty bottle and treated by oxygen to obtain the oxidized hydrogel. After 1 h, the oxidized hydrogel was obtained.

2.6. Rheological measurement

The rheological experiments were conducted to detect the complexation between the Fe(III) ions and the carboxylate groups of poly (acrylic acid) via storage modulus (G') on a rheometer (AR 2000ex TA America) with parallel plates (25 mm diameter rotating top plate). The samples were placed between the para-palates and the distance of plate-to-plate was 3 mm. The temperature was controlled at 25 °C. Dynamic frequency sweeps were carried out at

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