



Hierarchically crosslinked ionic nanocomposite hydrogels with ultrahigh mechanical properties for underwater bioinspired capturing device

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ABSTRACT

Various applications of nanocomposite hydrogels with a single crosslinked network have been largely limited by their poor comprehensive mechanical properties, despite their prominence in certain mechanical properties. Here, we introduce ferric ions into titania-based nanocomposite hydrogels to fabricate robust ionic nanocomposite hydrogels (INC gels) with hierarchically crosslinked networks. The introduction of ion crosslinkers into nanocomposite hydrogels dramatically improves their comprehensive mechanical properties. The mechanical attributes can be changed over wide ranges by adjusting hydrogel components and the optimal INC gel exhibits the super high strength of 13.0 MPa, elastic modulus of 26.8 MPa, and toughness of 34.3 MJ m⁻³. In addition, The INC gels show a good mechanical and volume stability in saline solutions due to the unique crosslinked network. The reversible phase separation in gels can be used for the achievement of the shape memory effect without significantly destroying the mechanical properties and enable the mussel shell-like hydrogel to imitate the self-protection behaviour of the mussel to grab the bead underwater. Therefore, these hydrogels will hold a great potential in underwater mechanical catching hands.

1. Introduction

Hydrogels as load-bearing materials have been employed in various fields such as soft actuators [1–3], sensors [4,5], tissue engineering [6,7]. All those applications often require hydrogels to own outstanding mechanical properties. For instance, hydrogels used for the artificial substitutes of biologic tissues and hydrogel electronic devices are usually needed to be able to withstand significant mechanical loads [8–10]. Besides the exceptional mechanical properties, the application of hydrogel in soft actuators, implantable medical devices and mechanical capturing hands also require the object materials to own shape-memory properties [11,12]. Other engineering domains such as oceanic antifouling also require hydrogels to remain mechanical and volume stability in a high salinity environment [13]. Thus, it is necessary to develop novel hydrogels with high strength, high stiffness, high toughness, good saline stability and shape-memory property together. So far, many attempts have been made to design and fabricate robust hydrogels, including nanocomposite hydrogels [14], double-network hydrogels [15], tetra-PEG hydrogels [16], polyampholytes hydrogels [17], macromolecular microsphere composite hydrogels

[18], and hydrophobically associated gels [19].

Among them, nanocomposite hydrogels (NC gels) generally consist of soft and hard segments, similar to the structure of certain biologic tissues. In the NC gels, uniformly dispersed inorganic nanofillers, acting as crosslink agents, are associated with flexible polymer chains by physical or chemical interactions to form a homogenous network structure [14]. Haraguchi et al. [14,20,21] used inorganic nanoclays as crosslink agents to prepare tough nanocomposite hydrogels with tunable mechanical, optical, thermal, and swelling properties via changing the nanoclay content. In general, increasing the clay content can further improve the mechanical properties of NC gels, whereas the high concentration of clays usually leads to an inadequate dispersion and in return negatively effects the mechanical attributes [22]. However, Jiang et al. [23,24] employed a vacuum filtration method to construct a lamellar structure with high clay content, which endowed nanocomposite hydrogels with a superior modulus that reached dozens MPa for layered clay nanocomposite hydrogels, and several MPa for layered clay-graphene oxide nanocomposite hydrogels. Furthermore, graphene oxide (GO) nanosheets as the crosslink agents also have been used to prepare tough nanocomposite hydrogels. The combination of GO

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nanosheets and polyacrylamide generated strong polyacrylamide/GO nanocomposite hydrogels with the tensile strength (385 kPa) [25], whereas using graphene peroxide (GPO) nanosheets as initiators and crosslink agents produced stronger GPO/polyacrylamide nanocomposite hydrogels with the tensile strength (> 1 MPa) [26]. In addition to the synthetic polymers, natural polymers also have been taken to fabricate tough GO-based nanocomposite hydrogels [27–29]. Alternatively, other nanomaterials such as metal oxide [30], hydroxyapatite [31] and silica [32] also have been adopted to synthesize strong and tough nanocomposite hydrogels. For instance, TiO_2 nanomaterials have been used for constructing tough nanocomposite hydrogels [30,33] and anisotropic hydrogels with an anti-vibration property [34], due to the high density of surface charges, high chemical stability, antibacterial property and non-toxicity [35,36]. In addition, the unique photocatalytic activity enable TiO_2 nanomaterials homogeneously dispersed in hydrogels to serve as UV-shielding devices and as a lasting photocatalytic crosslinker for further modulating the hydrogels [37,38]. For the NC gels, the contacts between polymer chains, significantly affecting the mechanical properties, are usually maintained by weak interactions. Although NC gels demonstrate an outstanding performance in certain mechanical properties, those gels rarely show an ideal combination of high strength, modulus and toughness.

Physical crosslinks formed by ionic bonds usually break and reform reversibly [39]. These reversible crosslinkers can effectively dissipate the external work upon breaking and restore the mechanical properties of hydrogels after forming again. Suo et al. [40] introduced Ca^{2+} ions into alginate/polyacrylamide hydrogels to prepare tough hybrid hydrogels with high fracture energy (ca. 9000 J m^{-2}). Gong and co-workers utilized ionic monomers to develop a novel physical hydrogels like rubber with high tensile strength (3.7 MPa), modulus (5.4 MPa), and toughness (14.8 MJ m^{-3}), however those gels exhibited a poor mechanical and volume stability in high salinity solutions [17]. The ionic crosslinkers from the low-valence (monovalent or divalent) cations are susceptible to the free cations in the saline [17,41], which leads to the breakdown of ionic crosslinkers. On the contrary, the ionic crosslinkers formed by high-valence (trivalent) cations not only show more stable in saline but also enhance the mechanical properties more than those from monovalent or divalent cations [42], due to the stronger interaction between trivalent cations and polymer chains [43]. Zhou et al. introduced ferric ions into chemically crosslinked hydrogels to obtain dual-crosslinked hybrid hydrogels with ultrahigh tensile strength (ca. 10 MPa), elastic modulus (ca. 17 MPa), toughness (ca. 26 MJ m^{-3}), and good self-recovery [44]. Based on the features of ionic crosslinks, the combination of nanocomposite networks and ionic crosslinks can effectively enhance the polymer interactions between polymer chains and improve the mechanical properties of the NC gels [45]. Recently several attempts have been made to combine nanocomposite networks and ionic crosslinks to generate tough hydrogels [46,47], whereas their tensile strength and elastic modulus are still lower than 10 MPa. Thus, there still is a challenge to achieve nanocomposite hydrogels with outstanding comprehensive mechanical properties.

In this paper, we fabricated tough ionic nanocomposite hydrogels (INC gels) by introducing ferric ions into titania-based nanocomposite hydrogels (NC gels). Here, the monomers containing acrylic acid (AA) and acrylamide (Am) in titania colloid solution were polymerized to fabricate NC gels with a single crosslinked network (nanocomposite network). Subsequently, the NC gels were immersed into ferric solutions and then into water to prepare INC gels with hierarchically crosslinked networks that endows INC gels with high strength, modulus, and toughness. Furthermore, the effect of the hydrogel components on the mechanical properties of INC gels has been systematically investigated. The optimal INC gels displayed the excellent comprehensive mechanical properties superior to articular cartilage and the good self-recovery. Besides the mechanical properties, the INC gels also exhibited an outstanding mechanical and volume stability in saline

solutions, irrespective of the NaCl content. The shape memory effect of INC gels could be achieved by reversibly controlling the phase separation in gels. Based on this memory effect and excellent mechanical properties, INC gels can be designed for mussel shell-like mechanical hands to grab a small object underwater.

2. Experimental section

2.1. Materials

Titania colloid (15% solid content) with the nanoparticle diameter of approximately 15 nm was purchased from Wanjing, China. Acrylic acid (AA), Acrylamide (Am), Iron nitrate nonahydrate, Potassium persulfate (KPS) were purchased from Bodi, China and N,N,N',N'-tetramethyldiamine (TEMED) was purchased from Sinopharm, China. All the chemicals were used as received without further purification. The water used in all experiments was purified by a Millipore Direct-Q purify.

2.2. Preparation of ionic nanocomposite hydrogel

Ionic nanocomposite hydrogels were synthesized by a two-step method. Firstly, Nanocomposite hydrogels were prepared according to our previous paper [30]. A polymer precursor solution including 5.5 g distilled water, 5.0 g TiO_2 colloid solution and monomers (AA and Am) was stirred and bubbled with nitrogen for 1 h to remove dissolved oxygen. Then the mixture was cooled to 0°C , followed by addition of 8 μL TEMED and 0.01 g KPS to the cooled solution. Finally, the precursor solution was transported into glass tubes and placed at 25°C for 24 h to form nanocomposite hydrogels (NC gels). Here, NC gels are denoted as AxAmyTz (x, y, and z refer to the molar percentage of AA in total monomers, the molar percentage of Am in total monomers, and the weight percentage content of TiO_2 in water).

Subsequently, the nanocomposite hydrogels were soaked in various ferric concentration solutions for 12 h and then placed in distilled water for 48 h with changing water every 8 h to prepare ionic nanocomposite hydrogels (INC gels). The INC gels are denoted as INC-AxAmyTz and the Ionic gels represent ionic-crosslinked hydrogels obtained by immersing the AxAmyTz hydrogels into ferric ions and later water. The samples for the shape memory were obtained by blending the straight INC gel specimens ($50 \text{ mm} \times 5 \text{ mm} \times 2 \text{ mm}$) into a spiral shape and then immersing them into ethanol at 20°C for 10 min to fix the temporary shape. The samples for capturing hands were prepared by fixing NC gels into the shell shape and soaking them in ferric solution and later water.

2.3. Sample characterization

Uniaxial tensile and compressive measures of hydrogels were employed on a Shimadzu ASG-J electronic universal testing machine at room temperature with the tensile speed of 100 mm min^{-1} and the press speed of 5 mm min^{-1} and the tests for each hydrogel were repeated at least six times. The elastic modulus of samples was established from the slope of stress-strain curves in the initial linear range, and the toughness of samples was determined from the area under the stress-strain curve. For the loading-unloading measurement, the sample surface was wrapped by silicon oil before testing and the crosshead speed was hold at 100 mm min^{-1} . The dissipation energy was obtained by integrating the closed area of stress-strain curve, while the dissipation ratio was defined as the ratio of closed area to the area under the loading curve during a loading-unloading test. The SEM images of fracture interfaces of hydrogels were obtained from the scanning electron microscope (Quanta 250, FEI Co., USA) at an accelerating voltage of 20 kV. The TEM images of the titania colloid and the hydrogel film were obtained from a transmission electron microscopy (JEOL JEM-2100F) and the ultrathin hydrogel film was prepared by a UC7 ultra-

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