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Bio-inspired layered chitosan/graphene oxide nanocomposite hydrogels with high strength and pH-driven shape memory effect

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ABSTRACT

The layered nanocomposite hydrogel films containing chitosan (CS) and graphene oxide (GO) have been prepared by water evaporation induced self-assembly and subsequent physical cross-linking in alkaline solution. The layered CS/GO hydrogel films obtained have a nacre-like brick-and-mortar microstructure, which contributes to their excellent mechanical properties. The tensile strength and elongation at break of the hydrogel films with 5 wt% GO are 5.35 MPa and 193.5%, respectively, which are comparable to natural costal cartilage. Furthermore, the CS/GO hydrogel films exhibited pH-driven shape memory effect, and this unique phenomenon is mainly attributed to the reversible transition of partial physically cross-linking corresponding to hydrogen bondings and hydrophobic interactions between CS polymer chains due to pH changing.

1. Introduction

Many soft tissues of human body and other animals such as cartilages, muscles, ligaments and corneas are mainly composed of biological gels with excellent mechanical properties and anisotropic structures (Calvert, 2010). In contrast, conventional synthetic hydrogels are mechanically weak due to the structural inhomogeneity in their network, and are generally isotropic in both microstructure and properties. Therefore, fabricating strong and tough hydrogels with anisotropic properties may expand their applications in artificial tissue engineering and the reconstruction of organs. Although some efforts have been made to introduce anisotropic structures in hydrogels with excellent mechanical properties, most of them have been focused on synthetic polymer-based hydrogels (Haque, Kamita, Kurokawa, Tsujii, & Gong, 2010; Wu, Kurokawa, Liang, Furukawa, & Gong, 2010; Wang, Lin, Cheng, & Jiang, 2012). Biopolymer-based hydrogels with high strength and anisotropic structure have rarely been reported (Nakayama et al., 2004).

Among various biopolymers, chitosan (CS) has been widely studied to prepare functional hydrogels for biomedical applications such as drug delivery, wound dressing, separation membranes, biosensors, and tissue engineering scaffolds due to their biocompatibility, low-cost and non-toxicity (Duan, Liang, Guo, Zhu, & Zhang, 2016; Tang, Du, Hu, Shi, & Kennedy, 2007; Yu, Bao, Shi, Yang, & Yang, 2017; Li et al., 2016; Duan, Liang, Cao, Wang, & Zhang, 2015; Chen et al., 2016). Chitosan-based hydrogel could be obtained by chemical cross-linking with aldehydes like glutaraldehyde (Ji, Khademhosseinib, & Dehghania, 2011) and physical cross-linking such as hydrogen bond interaction, electrostatic interaction, and hydrophobic interaction (Montembault, Viton, & Domard, 2005; Ladet, David, & Domard, 2008; Xu et al., 2016). For example, Yu et al. synthesized a high strength and high porosity hydroxyapatite/graphene oxide/chitosan composite hydrogel with good biocompatibility, those characteristics commendably meet the requirement of bone materials (Yu, Bao, Shi, Yang, & Yang, 2017).

However, the conventional chitosan hydrogel always shows weak mechanical properties, which severely hindered their practical applications in biomedical fields. Inspired by the unique “brick-and-mortar” hierarchical structure of nacre, extensive efforts have been devoted to fabricating high strength artificial composite materials (Walther et al., 2010; Ming, Song, Gong, Zhang, & Duan, 2015). The hierarchical architecture of nacre is constituted of the layered arrangement of inorganic aragonite platelets surrounded by a protein matrix, serving as glue between the platelets. The “brick-and-mortar” structure endows nacre with 1000-fold tougher than that of calcium carbonate. Therefore, platelet-like inorganic building blocks are essential elements in bioinspired composite materials with the superior mechanical properties. On the other hand, graphene and graphene oxide (GO) have attracted considerable attention as two-dimensional carbon nanomaterials with one atom thick in recent years owing to its extraordinary material properties (Zhu et al., 2010; Chen, Müller, Gilmore,

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Wallace, & Li, 2008; Terrones et al., 2011; Li, Han, Ling, Wang, & Sun, 2015). Thus, graphene nanosheets are the ideal candidates as the "bricks" for fabricating nacre-like composite materials (Li, Yu, Yang, Zheng, & Liao, 2012; Wang, Bai, Yao, Liu, & Shi, 2010; Sellam et al., 2015). For example, Liao and coworkers reported the preparation of nacre-like layered poly(vinyl alcohol)/graphene oxide composite films with excellent mechanical and conductive properties by solution-casting method (Li et al., 2012). Pan et al. illustrated that the Young's modulus, tensile strength, and elongation at break of the dry films are found to increase by 51% and 93% and 41% with the incorporation of only 1 wt% GO in CS matrix, respectively (Pan, Wu, Bao, & Li, 2011). However, using graphene nanosheets as a building block to prepare nacre-like composite films mostly focused on hard solid materials so far and relatively less has been reported on soft and wet hydrogel materials based on self-assembly process of graphene nanosheets as building blocks (Pan, Wu et al., 2011; Yang, Tu, Li, Shang, & Tao, 2010; Zuo et al., 2013). Hence, developing graphene-based nanocomposite hydrogels that possess the superior mechanical properties and unique layered nacre-like structure still remains a great challenge.

Here, we report the preparation of bio-inspired, nacre-like chitosan/graphene oxide (CS/GO) nanocomposite hydrogel films through a simple water evaporation induced self-assembly method followed by physical cross-linking in alkaline solution. The layered CS/GO hydrogel films exhibited high strength and toughness. Meanwhile, the strong and tough hydrogel films also showed the interesting pH-driven shape memory behaviors. Combined with outstanding mechanical properties and shape memory effect, their biocompatible properties make CS/GO hydrogel films promising candidates in biomedical applications such as artificial cartilages, tissue engineering and surgical devices.

2. Experimental

2.1. Materials

Chitosan (Mw = 500,000 g/mol, deacetylation degree ≥90%) was purchased from Shanghai Aladdin reagent Co., LTD (Shanghai, China). Natural graphite powder (325 meshes) was purchased from Qingdao Huarun graphite Co., LTD (Qingdao, China). All the other chemicals were products of Beijing Chem. Reagents Co., LTD (Beijing, China). They were used as received and all aqueous solutions were prepared using ultrapure water (18 MU) from a Milli-Q system (Millipore).

2.2. Synthesis of CS/GO composite hydrogels

Graphene oxide was prepared from graphite powder according to a modified Hummer's method (Geng & Jung, 2010; Kovtyukhova et al., 1999). It was purified by dialysis for one week to remove the remaining metal species. Finally, a stable dispersion of graphene oxide was obtained by ultra-sonication of the suspension in DI water.

Chitosan was dissolved in an aqueous solution of 1 wt% acetic acid to form a 2 wt% solution and it was kept for at least 24 h before use. Then the desired amount of GO solution (5 mg/mL) was added to the CS solution and stirred for 12 h. The resulting CS/GO mixtures were sonicated for 30 min and poured into Petri dish to let the water evaporate for the formation of hybrid films. The paper-like films were obtained by directly peeled off from the Petri dish. The contents of GO in CS/GO composite films were varied from 0 to 6 wt%, and the pure CS films were prepared according to the same procedure for comparison. The dried freestanding films were immersed in 1.0 wt% NaOH solution for 1 h to neutralize the extra acetic acid, and then washed in ultrapure water to remove the residual NaOH in the films. Finally, the CS/GO naocomposite films were further immersed in a large amount of ultrapure water for 4 h to reach the swollen equilibrium and then the CS/GO nanocomposite hydrogel films were obtained.

2.3. Characterization of GO and CS/GO composite films

The FTIR spectra of the samples were recorded in the range 4000–400 cm^{-1} using a Nicolet 6700 instrument (Thermal Scientific, USA) by the KBr method. The X-ray power diffraction (XRD) patterns were obtained on a Shimadzu X-ray diffractometer 6000 with Cu Ka radiation (λ = 1.5406 A°). The XRD patterns were recorded over the 2θ region of 5–50° with a scanning speed of 2°/min. SEM images were taken on a JSM 7401 scanning electron microscopy with the acceleration voltage of 20 kV. All the SEM samples were sputter-coated with gold before testing. AFM images were performed in tapping mode by using a Shimadzu SPM 9600. The thermal stability of the hydrogel films were carried out using a TA Instruments Q50 thermogravimetric analyzer (TGA) from 40 °C to 800 °C in a highly purified N_2 atmosphere with a heating rate of 10 °C/min. The tensile behavior of CS/GO composite hydrogel films were measured using a Shimadzu electronic universal testing machine ASG-J with a 100N load cell at a loading rate of 10 mm/min. All samples were cut into strips of 25 mm × 5 mm with a gauge length of 20 mm. For each composition, at least five specimens were tested in all mechanical measurements to obtain reliable values.

2.4. Measurement of swelling ratio of CS/GO hydrogel films

Swelling measurements were carried out with the dried CS/GO sample strips of 10 mm × 5 mm. The dried CS/GO films with different contents of GO were immersed in a large excess of ultrapure water at 25 °C, and weighed after removing the water on the surface by filter paper at set intervals. The swelling ratio (SR) was represented by the ratio of the weight of absorbed water in the hydrogel film to that of the corresponding dried sample.

$$SR = 100\% \times (Ws - Wd)/Wd,$$

where Ws is the weight of the swollen hydrogel and Wd is the weight of the corresponding dried hydrogel film.

2.5. Shape-memory behavior test

The shape-memory effect was evaluated according to a method described by Lendlein and Kelch (2002). A straight strip of the specimen (film size: 30 mm length, 3 mm width, and 0.130 mm thickness) was immersed into the aqueous solution at pH 3 for 5 min to soften the film. Then the composite was transferred to the aqueous solution at pH 12. It bent to an angle (θ_0) shortly afterwards due to the applied external force, and then kept the deformation for 10 min. A certain amount of bending angle (θ_d) dropped during unloading. Finally, the deformed specimen was immersed into aqueous solution pH 3 at room temperature (25 °C), and the change of the angle (θ_t) with time was recorded. The shape recovery ratio (R_r) was defined as follows:

$$R_r = 100\% \times (\theta_0 - \theta_t)/\theta_0,$$

And the shape fixity ratio R_f is then defined by

$$R_f = 100\% \times (\theta_0 - \theta_d)/\theta_0,$$

The macroscopic change of the shape with time was recorded using a digital camera.

2.6. Testing of the drug release behaviors

Hybrid films of chitosan with 5 wt% GO, served as drug carrier for drug release experiments were fabricated by a simple method described in 2.2. The wet samples were dried for 24 h at 60 °C for further research. After that, the resultant dry composites were deeply rinsed and kept in solutions containing salicylic acid (SA) which acted as a model drug for 90 min. Following these preparation steps, the films were dried and subsequently immersed in 100 mL of PBS (pH 5.8 and pH 7.4) and