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Lanthanide ions-induced formation of hierarchical and transparent polysaccharide hybrid films

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ABSTRACT

Nacre-like hybrid films based on *N*-succinyl chitosan (NSC), sodium alginate (SA) and lanthanide ions were fabricated via coordination interactions. In this work, the binary building blocks (NSC and SA) were self-assembled into aligned hydrogel films by coordination with lanthanide ions, and hierarchical NSC-SA hybrid films were obtained upon drying. Two species of lanthanide ions (Gd^{3+} and Yb^{3+}) were used to fabricate the hierarchical NSC-SA hybrid films. The as-prepared NSC-SA hybrid films exhibit high tensile strength and stability. The tensile strength and toughness of as-prepared hybrid films reach 122.10 MPa and 3.89 MJ m^{-3}, respectively. Meanwhile, the well-aligned lamellar microstructures also exhibit a good light transmittance. The highest light transmittance reaches 92% for NSC-SA hybrid films at 760 nm. This fabrication method for hierarchical NSC-SA hybrid films is innovative due to the utilization of rare earth coordination bonding, and can serve as the basic strategy for the construction of high-performance composites in the near future.

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1. Introduction

In the last decade, there has been a trend in the design of advanced materials by mimicking natural materials. For example, seashell nacre and bones have good mechanical strength and toughness complemented by unique biological and biomedical properties, inspiring a new strategy for the fabrication of high-performance and multifunctional materials (Ben-Nissan, 2003; Cui et al., 2014; Palin, Liu, & Webster, 2005; Swetha et al., 2010; Yao, Tan, Fang, & Yu, 2010). Very recently, several innovative techniques have been reported to fabricate the artificial nacre-like materials including vacuum filtration (Yao et al., 2010), covalent bonding (Cheng, Wu, Li, Jiang, & Tang, 2013), layer-by-layer (LBL) assembly (Finnemore et al., 2012), ice-crystal templates (Munch et al., 2008) and water-evaporation (Li, Yu, Yang, Theng, & Liao, 2012). For instance, nacre-like graphene oxide (GO) and gellan gum (GG) composite films were prepared by vacuum filtration (Kang, Cai, Jin, & Zhang, 2015). Poly(vinyl alcohol)/montmorillonite (MTM) nacre-like nanocomposites with a tensile strength of up to 400 MPa were prepared via LBL deposition (Podsiadlo et al., 2007). A brick-and-mortar Al_2O_3/poly(methyl methacrylate) composite film was formed by ice-crystal templates (Munch et al., 2008). Nacre-like structural MTM–chitosan nanocomposites were fabricated by water-evaporation induced self-assembly (Yao et al., 2010). However, most of these nanocomposites films are fabricated by physical or hydrogen bond interactions. There are seldom reports on the preparation of artificial nacre-like nanocomposite film with high mechanical strength via metal coordination interactions.

In recent years, lanthanides have attracted great attention due to their coordination ability and luminescence characteristics (Bol, van Beek, & Meijerink, 2002; Karraker, 1967). Lanthanides coordinated-polymeric materials also exhibit mechanical flexibility, good chemical stability and excellent process ability (Pan, Huang, Li, Wu, & Zheng, 2000; Yang et al., 2006). For example, Pan et al. synthesized single- and double-layer and three-dimensional structures of rare-earth metal coordination polymers (Pan et al., 2000). Yang et al. reported the preparation of 2D and 3D rare-earth coordination polymers with photoluminescence, up-conversion and magnetism (Yang et al., 2006). These rare-earth metal coordination polymers exhibit specific structure or excellent physical properties.

Herein, two kinds of organic biopolymers, *N*-succinyl chitosan (NSC) and sodium alginate (SA) were used as building blocks to fabricate the hierarchical hybrid films. Chitosan is a natural polysaccharide with many excellent properties, including bio-

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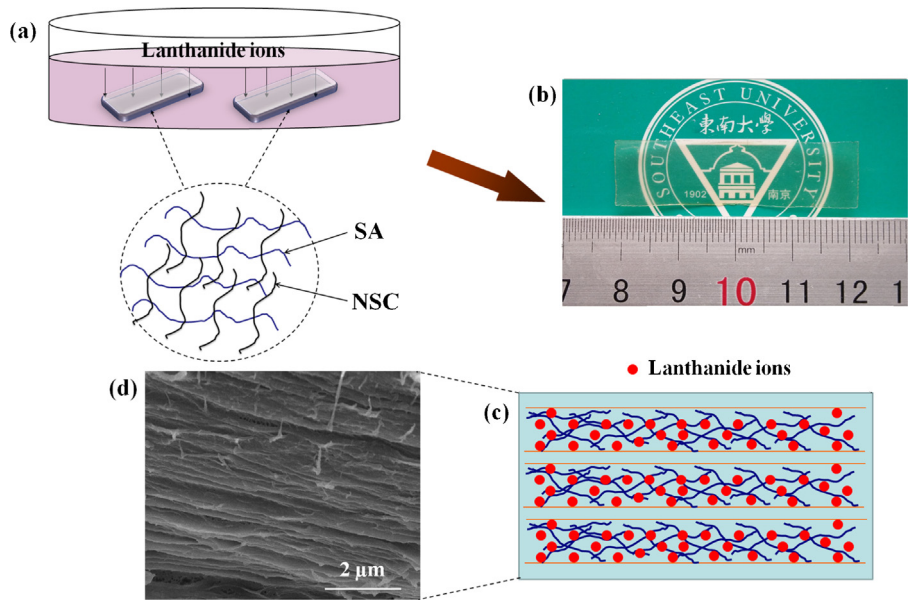

Scheme 1. (a) Fabrication process of nacre-like hierarchical NSC-SA hybrid film; (b) digital photograph of the nacre-like hierarchical NSC-SA hybrid film; (c) the interaction between NSC and SA is generally regarded as multiple lanthanide ions coordination and hydrogen bonds interaction; (d) cross-sectional morphology of the nacre-like hierarchical NSC-SA_3-Yb hybrid film.

compatibility, non-toxicity and biodegradability, etc (Agnihotri, Mallikarjuna, & Aminabhavi, 2004; Mørch, Donati, Strand, & Skjåk-Bræk, 2006; Papageorgiou et al., 2010; Rinaudo, 2006). NSC is derived from chitosan via introduction of succinyl groups at the *N*-position of chitosan with abundant carboxyl groups (Bashir, Teo, Ramesh, & Ramesh, 2016). Because of its water solubility, biocompatibility and low toxicity, there has been a growing interest to develop NSC-based composite materials (Tan, Chu, Payne, & Marra, 2009). Alginate, a seaweed-derived linear unbranched polysaccharide containing repeating units of 1,4-linked α-L-guluronic acid and β-D-mannuronic acid, is one of the most common natural materials used to fabricate alginate-based composite materials (Zlopasa, Norder, Koenders, & Picken, 2015). NSC-SA building blocks were self-assembled into hydrogel films using lanthanide ions to coordinate the carboxyl groups in NSC and SA, followed by drying to obtain hierarchical NSC-SA hybrid films. Two species of lanthanide ions (Gd^{3+} and Yb^{3+}) were investigated to fabricate the hierarchical NSC-SA hybrid films. The fabrication process is simple, fast and easily scaled up.

2. Materials and methods

2.1. Materials

Sodium alginate (CAS No. 9005-38-3, MW ~ 20–40 kDa) and succinic anhydride were purchased from Aladdin Industrial Corporation (Shanghai, China). Chitosan powder was supplied by Lianyungang Biologicals Inc. (China), and has a deacetylation degree of 90% and viscosity-average molecular weight of 20,000 Da. $Gd(NO_3)_3{\cdot}6H_2O$ and $Yb(NO_3)_3{\cdot}6H_2O$ were purchased from Aladdin Industrial Corporation. All other reagents were analytical grade and used without further purification.

2.2. Preparation of NSC

NSC was synthesized according to the previous reported method (Aiping, Tian, Lanhua, Hao, & Ping, 2006). In brief, 1 g of chitosan was dissolved into 100 mL of 1 wt% HAc solution and the solution was transferred into a flask. Succinic anhydride (0.2 g) was dissolved in acetone (20 mL), and added into the flask dropwise for 30 min at room temperature. The reaction was allowed to stir at 40 °C for 4 h. The reaction mixture was cooled to room temperature. The mixture was precipitated into an excess of acetone. The precipitates were filtered and washed in succession with 70%, 80%, and 100% acetone. Finally, the product was dried at 40 °C under vacuum for 24 h.

2.3. Preparation of NSC-SA hybrid solution

Aqueous NSC solution (4 wt%) was obtained by adding the NSC powder into deionized water, followed by stirring at room temperature for 2 h. Aqueous SA solution (4 wt%) was obtained by adding the SA powder into deionized water, followed by stirring at 50 °C to fully dissolve. NSC-SA hybrid solution was obtained by mixing the NSC and SA solutions with different volume ratios. A series of NSC-SA hybrid solutions were obtained with volume ratios of 4:1, 2:1, 1:1, 1:2, and 1:4. These hybrid solutions were named as NSC-SA_1, NSC-SA_2, NSC-SA_3, NSC-SA_4, and NSC-SA_5.

2.4. Preparation of NSC-SA hybrid hydrogel films

NSC-SA hybrid hydrogel films were obtained from NSC-SA hybrid solutions via lanthanide ions coordination. In brief, NSC-SA hybrid solution was injected into a rectangle mold (50 × 20 × 0.5 cm in length, width and depth) and carefully immersed in Gd^{3+} (or Yb^{3+}) ions solution (0.05 mol L^{-1}). The hydrogel film was allowed to form at room temperature for 6 h. The hydrogel film was immersed in deionized water for 2 days to remove the free lanthanide ions. The NSC-SA hybrid film was obtained by drying the NSC-SA hybrid hydrogel film at 50 °C for 12 h. The hybrid films prepared from Gd^{3+} and Yb^{3+} ions were referred as NSC-SA-Gd and NSC-SA-Yb hybrid films, respectively. Pure NSC and SA hybrid films were prepared by the above method as a control.

2.5. Characterization

FTIR spectra were recorded from samples in KBr pellets using a Nicolet 5700 FTIR instrument in the range of 400–4000 cm^{-1}. X-ray diffraction (XRD) measurements were carried out at room temperature by using an Ultima IV diffractometer made by Rigaku

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