Chemical Engineering Journal 321 (2017) 502–509

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Zinc ions enhanced nacre-like chitosan/graphene oxide composite film with superior mechanical and shape memory properties

Shunli Liu [a], Fang Yao [a], Olayinka Oderinde [a], Kewen Li [a], Hongjiao Wang [a], Zhihong Zhang [b,*], Guodong Fu [a,*]

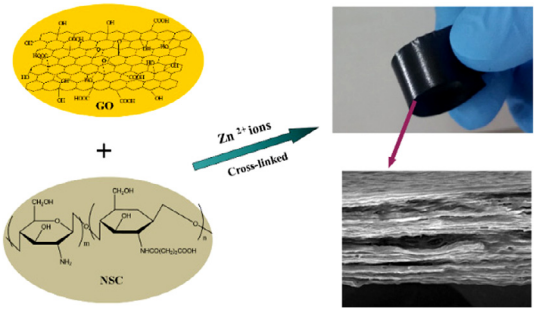
[a] School of Chemistry and Chemical Engineering, Southeast University, Jiangning District, Nanjing, Jiangsu Province 211189, China
[b] Henan Provincial Key Laboratory of Surface and Interface Science, Zhengzhou University of Light Industry, No. 166, Science Avenue, Zhengzhou, Henan Province 450002, China

HIGHLIGHTS

- Nacre-like composite film based on N-succinyl chitosan and graphene oxide was fabricated by zinc ions cross-linked.
- Zinc ions enhanced the mechanical properties and stability of the hierarchical NSC/GO-Zn composite film.
- Unique shape memory response to alcohols and bactericidal property was revealed.

GRAPHICAL ABSTRACT

Nacre-like chitosan-graphene oxide film with superior mechanical performance, high stability, bactericidal property, and shape memory were fabricated.



ARTICLE INFO

Article history:
Received 7 November 2016
Received in revised form 18 March 2017
Accepted 18 March 2017
Available online 20 March 2017

Keywords:
Hierarchical film
N-succinyl chitosan
Graphene oxide
Zinc ions cross-linking
Shape memory

ABSTRACT

Bio-inspired by the hierarchical structure and remarkable mechanical properties of natural nacre, nacre-like N-succinyl chitosan (NSC)-graphene oxide (GO) composite film was fabricated via zinc ion cross-linking and evaporation process. NSC and GO were used as the building "mortar and bricks," which rapidly self-assembled into composite hydrogel (NSC/GO-Zn) via zinc ions cross-linking, and the hierarchical NSC/GO-Zn composite film was obtained thereafter by evaporation. A series of NSC/GO-Zn composite films with different GO concentrations was fabricated with the layered structure, as confirmed by scanning electron microscopy. Zinc ion-enhanced hierarchical NSC/GO-Zn composite film exhibited remarkable mechanical properties (strength of 212.6 ± 10.1 MPa and toughness of 2.51 ± 0.08 MJ·m^{-3}). Unique shape memory response to alcohols was demonstrated by the composite film due to the presence of the chitosan, which has a significant ability to desorb/absorb water. Furthermore, a remarkable broad-spectrum bactericidal property of the NSC/GO-Zn composite film was observed through *E. coli* and *S. aureus* exposure. These features indicated that NSC/GO-Zn composite film has inherent properties that can be used in protection, aerospace, and biological materials.

1. Introduction

Recently, considerable attention has been devoted to fabricate high-performance and multi-functional materials [1–4]. Bio-inspired by the unique hierarchical structure and excellent mechanical properties, a variety of methods, including water-evaporation, ice-crystal-template, layer-by-layer, and vacuum-assisted flocculation, are presently being used in the fabrication of nacre-like hierarchical composites [5–9], which were found to have unique hierarchical structure and excellent mechanical properties [10–13]. For example, a kind of nacre-like film based

* Corresponding authors.
E-mail addresses: mainzhh@163.com (Z. Zhang), 101010855@seu.edu.cn (G. Fu).

http://dx.doi.org/10.1016/j.cej.2017.03.087
1385-8947/

on binary hybrid graphene oxide/sodium alginate with excellent qualities has been fabricated by Chen et al. [14], whereas electrically conductive and mechanically strong biomimetic chitosan/reduced graphene oxide composite film was reported by Wang et al. [15]. However, some of these composite films were formed through weak hydrogen bonds with low stability and easy decomposition under water or saline solution. Enhancement of the stability of nacre-like composite film to broaden its applications under different conditions, such as high temperature or humid environment, is therefore necessary.

Chitosan, a polysaccharide derived from deacetylation of chitin, exhibits numerous interesting physicochemical and biological properties because of its good biocompatibility, biodegradability, and multiple functional groups [16–18]. However, poor water solubility of chitosan restricts the wide applications. To improve the solubility of chitosan, introduction of carboxyl groups at the N-position of the glucosamine units has been documented as an effective method. Due to its low toxicity and biocompatibility, N-succinyl chitosan (NSC) was investigated and synthesized via introduction of succinyl groups at the N-position of chitosan [19,20].

Graphene is a strong 2D carbon material that exhibits extraordinary electrical and mechanical properties for various applications [21,22]. The graphene derivative, graphene oxide (GO) is a potential candidate for fabricating composite materials because of its surface functional groups, including carboxyl, hydroxyl, and epoxy groups. Many works have been devoted to fabricating ultra-strong GO-based composite films, such as GO-gellan gum composite film with a fracture strength of 88.7 MPa and a tensile modulus of 25.4 GPa [23], and GO-poly(dopamine) composite film formed through synergistic hydrogen and covalent bonds [24].

To achieve nacre-like composite materials with high-performances, one of the most popular strategies is to introduce metal ions into the internal structure to form coordination bonds, leading to significant improvement of the mechanical properties and stability [25,26]. Herein, NSC, GO, and zinc ions were selected as the ideal candidates for preparing nacre-like NSC-GO-Zn composite films. The building "matrix and bricks" of NSC and GO were rapidly self-assembled into composite hydrogel via zinc ions cross-linking, and the hierarchical NSC/GO-Zn composite film was obtained thereafter by evaporation. Zinc ion-enhanced hierarchical NSC/GO-Zn composite film exhibited remarkable mechanical strength and shape memory properties. Furthermore, remarkable stability and broad-spectrum bactericidal property of the hierarchical NSC/GO-Zn composite film were observed.

2. Experimental

2.1. Materials

Chitosan (deacetylation degree of 0.95 and viscosity of 100-200mpas) was obtained from Shanghai Macklin Biochemical Co. Ltd. (Shanghai, China). Succinic anhydride was purchased from Aladdin Industrial Co. Ltd. (Shanghai, China). Sodium carbonate anhydrous and $ZnCl_2$ were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All other reagents (e.g. $KMnO_4$, H_2SO_4, $NaNO_2$, CH_3OH, C_2H_5OH, and C_4H_9OH) were analytical grade and used without further purification.

2.2. Preparation of GO and NSC

Graphene oxide was prepared by the modified Hummers method [27,28]. Different concentration of colloidal GO dispersion was prepared by suspending the as-prepared GO in deionized water and ultra-sonicated for 60 min. The synthesis of NSCS was carried out based on a method previously reported by Bajpai et al. [18]. In a typical experiment, chitosan powder (2.0 g) was added to deionized water (200 mL) with magnetic stirring for 1 h at room temperature. Succinic anhydride (1.13 g) and sodium carbonate anhydrous (0.95 g) were mixed uniformly and added to the reaction system every 30 min for four times. The resulting mixed solution was stirred continuously for the next 4 h at room temperature. Afterwards, pH was adjusted to 10 with 1 mol L^{-1}NaOH solution while the unreacted chitosan was precipitated out by centrifugation. The mixing solution was thereafter precipitated in an excess of ethanol and filtered to remove the solvent. The resulting product was washed with water and further precipitated in an excess of acetone three times. The product was then dried in vacuum at 40 °C for 6 h. Aqueous NSC solution (5 wt%) was obtained by adding the NSC power into deionized water, after which it was stirred for 1 h. NSC and GO hybrid dispersions were prepared by incorporating a GO dispersion into NSC solution with equivalent volume.

2.3. Fabrication of hierarchical NSC/GO-Zn composite film

Nacre-like NSC/GO-Zn composite film was obtained from NSC/GO-Zn composite hydrogel by via evaporation. In brief, NSC/GO hybrid dispersion was injected in a rectangle mold ($50 \times 20 \times 0.5$ cm in length, width and height) and carefully immersed in 0.02 mol L^{-1} zinc ions solution. The hydrogel formation was enhanced by the zinc ions cross-linking reaction for 12 h at room temperature. The hydrogel body was later rinsed in deionized water several times and evaporated at 60 °C for 12 h. A series of NSC/GO-Zn composite films with different GO concentrations were obtained, including NSC/GO-Zn_1 (GO, 2.5%), NSC/GO-Zn_2 (GO, 5%), NSC/GO-Zn_3 (GO, 10%) and NSC/GO-Zn_4 (20%).

2.4. Characterization

Field emission scanning electron microscope (FE-SEM) was carried out with the JSM-6490LV scanning electron microscope (Japan).X-ray diffraction (XRD) spectra were acquired using a D8 Advance X-ray diffraction instrument (Germany) with the scanning 2θ angle of 5° to 80°. Fourier-transform infrared (FTIR) spectra were recorded from samples in KBr pellets using a Nicolet 5700 FTIR instrument in the range of 400 to 4000 cm^{-1}.TGA curves of the films were obtained by Shimadzu TGA-50 thermogravimetric instrument. The temperature range employed is from 50 to 600 °C with a ramp rate of 10 °C min^{-1}.

Furthermore, mechanical properties were measured using a Shimadzu AGS-X tester with gauge length of 5 mm and loading rate of 1 mm/min. All measurements were conducted at room temperature. Hierarchical NSC/GO-Zn samples with the thickness ~0.2 mm were cut into strips with the width of 5 mm and length of 10 mm. The toughness was calculated by the area under the stress-strain curves. The mechanical properties for each sample are based on the average value of 5 specimens.

2.5. Swelling behaviors (SR) of the NSC/GO-Zn composite film

The swelling ratio of NSC/GO-Zn composite film was measured by the weighing method at room temperature. In detail, pre-weighed dry NSC/GO-Zn composite film were immersed in aqueous solution until swelling equilibrium. Thereafter, excessive