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Green synthesis of silver nanoparticles impregnated bacterial cellulose-alginate composite film with improved properties

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ABSTRACT

Bacterial cellulose (BC) has attracted more and more attentions as a biomedical material. However, pure BC possesses a poor mechanical strength in a wet state, a weak water swelling ability after drying as well as no antibacterial activity. To resolve this, a kind of novel silver nanoparticles (AgNPs) impregnated bacterial cellulose/calcium alginate (BC/CA) composite film was fabricated for the first time using a new form of BC/CA double-network (DN) film as the template to in situ synthesize AgNPs by a facile method, UV irradiation. This composite realized obvious improvements in both the mechanical property (fracture strength and fracture strain) and the water swelling ability, with values of 2.97, 1.41 and 4.08 times, respectively, those of pure BC, as well as a high and prolonged antibacterial effect for more than 48 h.

1. Introduction

Bacterial cellulose (BC) is a type of natural cellulose synthesized by microorganism. It features some distinguished physical properties, e.g. high porosity, excellent water holding capacity and good biocompatibility, making it widely used as a building block for biomedical materials [1] and composite materials [2]. However, pure BC film possesses a poor mechanical strength in a wet state, a weak water swelling ability after drying as well as no antibacterial activity [3]. To resolve this, many researchers tried to combine BC with inorganic or organic compounds, such as Laponite clay [4] and gelatin [5,6]. But, these BC based composite films were tough to improve both the mechanical strength and water swelling ability, unless an extra crosslinking treatment was involved, in which a high cost of crosslinking regent like transglutaminase or genipin was used [6].

Alginate is a natural linear polysaccharide and widely used as biomedical materials [7]. Until now, some methods have been reported to prepare BC/alginate composites. Generally, these methods could be classified into two types. One was adding alginate into the culture medium during BC's biosynthesis procedure [8]. The other was crushing BC film into slurry and mixing it with alginate solution, followed by coagulation with $CaCl_2$ [9–11]. However, these reported BC/CA composites usually had a weaker mechanical strength than pure BC [9–11]. We thought that this decrease was mainly attributed to the damage of BC's network microstructure. Based on this, in this work, we intended to use an intact BC film, instead of BC slurry, to prepare a BC/CA double-network composite. This method was expected to maintain the natural three-dimensional network structure of BC, thus realizing an improvement in both the mechanical strength and water swelling ability. As far as we know, no such works have been reported yet.

Furthermore, in order to satisfy the demands of antibacterial effects in biomedical applications, the BC/CA DN composite film was utilized for the first time as the template to in situ synthesize silver nanoparticles (AgNPs) by an environmental friendly method, UV irradiation. Silver nanoparticles are one of the most effective antibacterial agents because of their large surface area to volume ratio as well as surface plasmon resonance [12]. In our previous work, we have explored a silver nanoparticles impregnated bacterial cellulose (AgNPs-BC) nanocomposite by chemical reduction [13] and hydrothermal treatment [14], respectively. It was found that the BC film was a good template for in situ synthesis of AgNPs. Herein, the effects of the templates on the formation of AgNPs and their antibacterial activities were compared between pure BC and BC/CA DN composite film.

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2. Materials and methods

The preparation of BC films was preformed according to our previous work [14]. For the synthesis of BC/CA DN composite, the BC film was partially dehydrated and immersed in sodium alginate (SA, Sinopharm Chemical Reagent Co., Ltd, China) aqueous solution (1.0 w/v%) at 80 °C for 6 d. Then, this film, called as BC/SA composite, was picked out and further cross-linked by immersing it into a $CaCl_2$ solution of 4 w/v% for 2 d.

The BC/CA DN composite was utilized as the template to in situ synthesize AgNPs. Typically, one piece of the BC/CA film was immersed into 50 ml, 1 mM $AgNO_3$ solution under agitation at 100 rpm and 30 °C for 12 h protected from light. Then it was picked out and exposed to a UV lamp (wavelength = 254 nm, 30 W) for another 4 h. Finally, the film was washed with 3 × 10 ml of distilled water to remove the excess chemicals. The pure BC was also utilized as the template using the above-mentioned method.

The characterization of BC, BC based composites and AgNPs were performed according to our previous works [14,15]. For the measurement of water swelling ratio, the films were first dried at 105 °C for 24 h and weighted with the weight noted as M_1. Then, they were immersed in distilled water at 25 °C for another 24 h. The re-swollen films were picked out and weighted accurately with the weight noted as M_2. The water swelling ratio (folds) = $(M_2 - M_1)/M_1$.

Two methods, i.e., the zone of inhibition and dynamic shake flask method were adopted to evaluate the antibacterial activity according to our previous work [13]. The long-term antibacterial property of the AgNPs-BC/CA composite was investigated by determination of the growth curve of *E. coli* in the culture medium containing the films [14]. After 24 h, the same amount of fresh bacterial suspension was reinoculated, and incubated for another 24 h.

3. Results and discussion

The BC film has been proved a good template for in situ synthesis of AgNPs [13,14]. Although these AgNPs-BC composites exhibited high antibacterial activities, they still possessed a poor mechanical strength in a wet state and a weak water swelling ability after drying. To resolve this, a BC/CA DN composite was produced by combining the BC film with calcium alginate (CA) (Fig. 1). Compared with other reported BC/CA composites, its feature was that an intact BC film, instead of BC slurry was utilized as one component [9–11], and the DN composite maintained the BC's network microstructure well (Fig. 1). Besides, the physical crosslinking resulted in the differences of the microstructures between BC/SA and BC/CA DN composites. Both materials possessed thicker microfibrils than pure BC, while the BC/SA composite had no obvious layer structure in the BC network. The AgNPs were in situ synthesized in the BC/CA DN composite, using an environmentally benign and facile approach, UV irradiation. In this process, no chemical reagents were introduced because the BC/CA films could act as a reducing regent due to the existence of many hydroxyl groups on their microfibrils. As shown in Fig. 1, the color of the BC/CA DN composites turned from white to dark yellow, signifying the formation of AgNPs [13,14].

Table 1 listed some mechanical and physical properties of BC and its composites. The pore volume of the BC/CA composite was much smaller than that of BC. This result was consistent with that by SEM observations. The BC/CA composite obtained obvious enhancements in the fracture strength and fracture strain, which were 3.22 and 1.26 times, respectively, those of BC, followed by the BC/SA composite, which were 1.76 and 1.07 times, respectively. It could be concluded that the mechanical strength of the BC/CA composite was improved mainly due to the crosslinking of SA. The reasons behind this phenomenon might be attributed to the unique structure of DN composites, which supplied an effective relaxation of locally applied stress and dissipation of the crack energy by combinations of two networks [16]. As far as we know, this BC/CA DN composite had a superior mechanical property than previously reported BC/CA composites. For example, Kanjanamosit et al. synthesized a bacterial cellulose-alginate film by fermentation using a culture medium containing SA. This composite reserved only 72% of fracture strength and 69% of fracture strain of pure BC [17]. Chiaoprakobkij et al. synthesized a BC/CA blend film by mixing the BC slurry with SA solution, followed by treatment with $CaCl_2$. Compared with pure BC, this composite showed a decrease in mechanical properties, i.e., about 75% of fracture

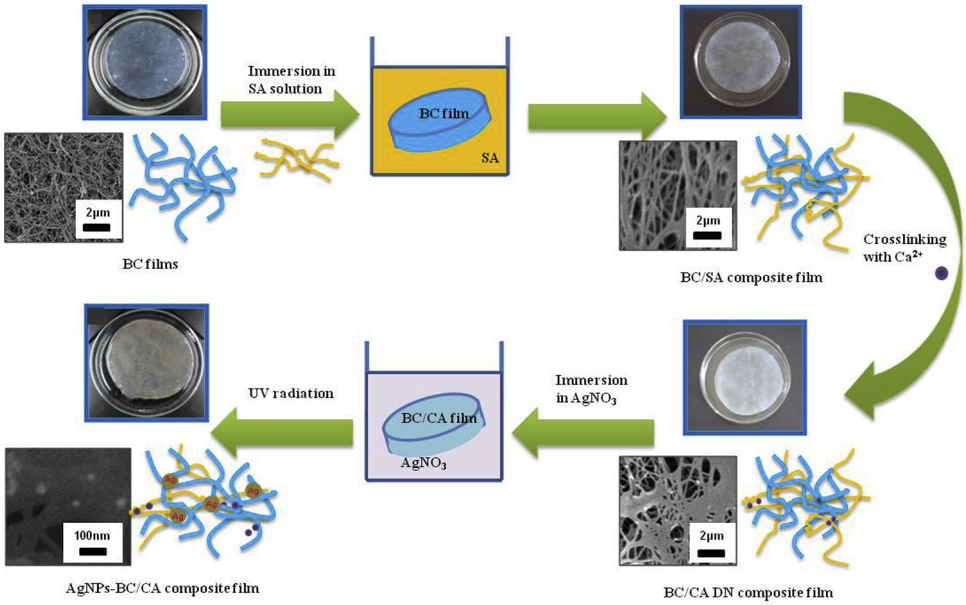

Fig. 1. Schematic illustration of the fabrication process of AgNPs-BC/CA composite film including the photographs and SEM images of BC, BC/SA, BC/CA DN composite film and the photograph and FE-SEM image of AgNPs-BC/CA composite film.