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Controlled formation of surface hydrophilicity enhanced chitosan film by layer-by-layer electro-assembly

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ABSTRACT

Several surface hydrophilicity enhanced chitosan, CS, films were controllably formed by using the layer-by-layer electro-assembly, LBLEA, method with varied voltages. Experimentally, an employed electrostatic generator was employed by taking its anode and cathode electrodes alternatively linking to the CS solution or silicon plate to form two opposite cycles corresponding to the electrostatic force, EF, enhancement or reduction, respectively. Wetting results showed that the water contact angle, θ_W, on those CS film surfaces was gradually reduced with the applied voltage increase, especially by EF reduction, e.g. the θ_W on 0 V sample at about 55° and on 4 kV EF-reduction formed sample at about 20°. AFM images comparison showed that the LBLEA process can control the surface structure for CS film. ATR–FTIR spectra comparison showed that the EF reduction process would reveal the C–O groups on CS film surface to enhance the hydrophilicity.

1. Introduction

Chitosan, CS, is derived by de-acetylating of chitin. CS is the second most abundant biopolymer in nature after cellulose [1,2]. CS has special β(1 → 4) linked D-glucosamine structure and this leads it has some important advantages, e.g. biocompatibility, biodegradability and notoxicity [1–5]. CS is a positive polyelectrolyte with bad hydrophilic due to the water contact angles, θ_W, on its surface at about 50–60° [6–10]. This thus limited its application due to somewhere the used CS is wished to have either enhanced hydrophilic or in hydrophobic [10–14].

As known, the surface properties of CS can be modified by chemical [2] or physical methods, e.g. the UV irradiation [15] and the low-energy electron irradiation [16]. Our recent study showed that the hydrophilic CS surface can be turned into hydrophobic by layer-by-layer electro-assembling, LBLEA, the negative lignosulfonate [5]. However, it is truly yet without a method can be directly applied fabrication of CS film with controlled hydrophilicity.

In this work, we introduced a case to directly fabricate the CS film with enhanced hydrophilicity. Experimentally, we again used the LBLEA method, however, only the CS was used. As the same as previously, the anode and cathode electrodes of the electrostatic generator were alternatively linked to the positive CS solution and the used silicon plate to form two opposite cycles in relation to the electrostatic forces, EF, in enhancement or reduction, respectively [5].

2. Materials and methods

2.1. Materials

A commercial CS powder in microsize (Weifang Kehai Chitosan Co., Ltd, China) was used as received. In terms of the provider, this CS has a molecular weight of about 3×10^5 g/mol and a de-acetylation degree of about 95%, respectively [5].

2.2. Formation of chitosan film by layer-by-layer electro-assembly

The CS solution was prepared by dissolving the CS powder in acetic acid at a concentration of 2 mg/ml and pH at 4.1, respectively [5]. During the assembly process, a single crystal silicon plate (Zhejiang Crystal-Optech Co. Ltd. China) was used and pretreated as the same as previously [5].

The EF-controlled LBLEA process was performed as Fig. 1 described by taking the anode and cathode electrodes alternatively to link to either the positive CS solution or the silicon plate, respectively. In presented two cycles, the linkage presented as Fig. 1 left described by inserting the anode electrode into the positive CS solution should cause the occurred EF in enhancement, and the linkage described as Fig. 1 right should correspond to the EF reduction. By varying the applied voltages, therefore, the EF enhancement or reduction would be controlled in formation of those CS films.

During this electro-assembly process corresponding to different applied voltages, the substrate was immersed in CS^+ solution for each run and each run was kept about 10 min at 25 °C, then air dried for next running under an air stream flow condition.

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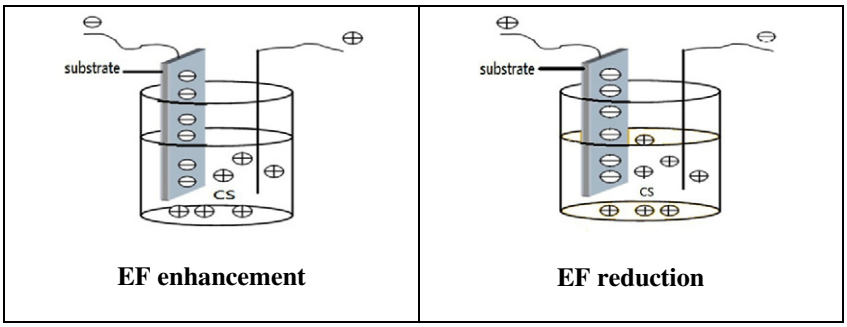

Fig. 1. Scheme on the formation of CS film by LBLEA in relation to the control of the EF in enhancement or reduction, respectively.

2.3. Characterization

The wetting was performed by means of the sessile drop contact angle measurement using the OCA40 Micro (Dataphysics Co., Ltd). During the measurement, the droplet volume was controlled constantly at about 1 μl for each drop and the temperature was controlled in constant, 25 °C.

The surface topography and roughness of the multilayer film were analyzed using a NanoScope IV (Veeco Co., Ltd) atomic force microscopy, AFM, with a tapping mode.

The attenuated total reflectance Fourier transform infrared spectroscopy, ATR–FTIR, (NEXUS-670, Nicolet Co., Ltd) was applied to present spectra in transmission mode by aligning the film on a silicon wafer substrate (1–2 cm^2) at a Brewster's angle of 75° with respect to the incident beam.

3. Results and discussions

3.1. Effect of applied voltages on the wettability and morphology of chitosan films

To enhance the hydrophilicity of CS seems to be not easy because Praxedes et al. have applied the UV irradiation to treat CS [15]. In terms of them, the θ_W on CS surface was reduced very few because the original surface presented value at about 85° and after UV irradiation reduced to at about 75° [15]. In addition, the electro-deposition enhanced the hydrophilicity of CS was also found few [17].

The wettability of LBLEA formed CS films in relation to various applied voltages was showed in Fig. 2. We found that the water contact angle, θ_W, on these CS films obviously reduced because it on 0 V sample surface at 55.3 ± 1.00° in good agreement with our previous report [5]

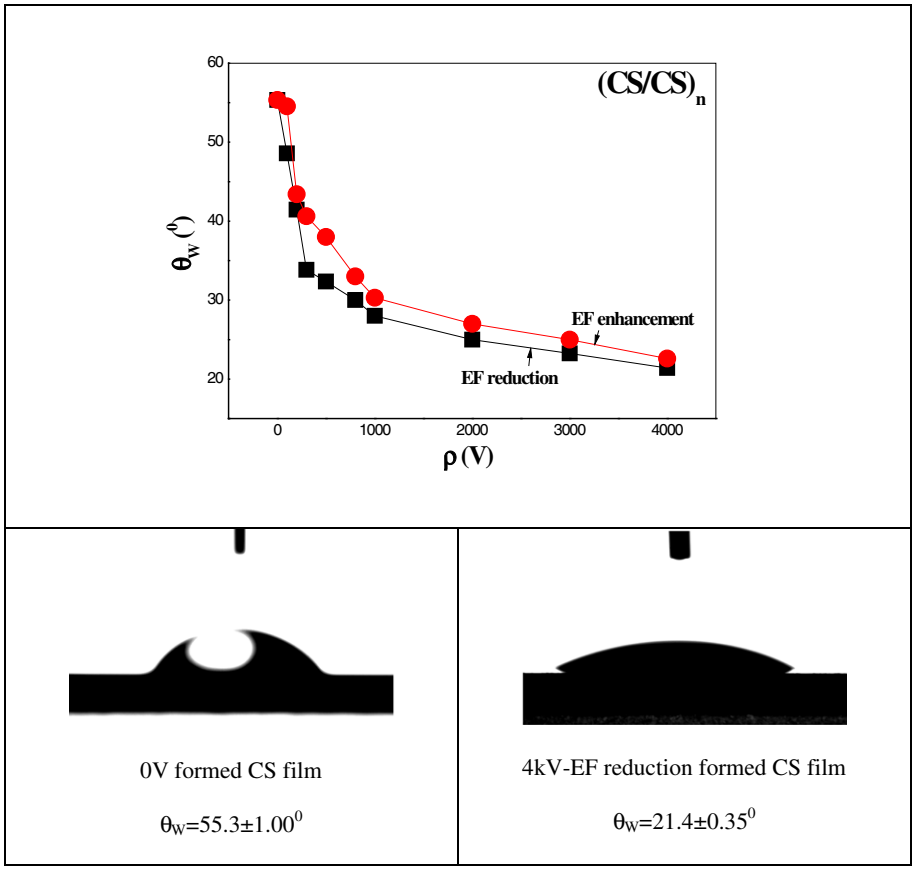

Fig. 2. Wettability of the LBLEA formed CS films in relation to the EF enhancement or reduction, respectively.