Influence of Operational Parameters on Layer-by-layer Assembled Cellulose Derivatives Thin Film

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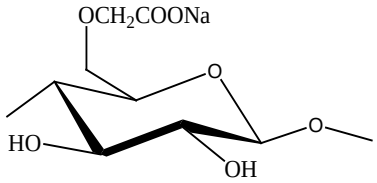
Abstract. Positively charged cellulose derivative quaternized cellulose (QC), was layer-by-layer (LbL) assembled with negatively charged cellulose derivative carboxymethyl cellulose (CMC) to produce the thin film. The factors of dipping and rinsing time on the thin film growth were investigated. FT-IR confirmed that QC and CMC can be layer by layer assembled in different dipping and rinsing time. As dipping time increases, the thickness of fabricated QC/CMC thin film will increase, while increasing rinsing time leads to decrease in the thickness of the QC/CMC thin film.

Introduction

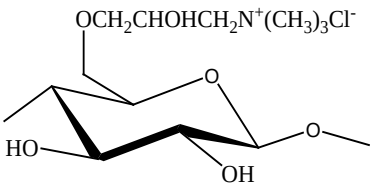
Layer-by-Layer (LbL) assembly, developed by Decher et al. in the 1990s, has been proven to be a simple but effective way to prepare thin films, coatings, or microcapsules with fine-tuned structures and components, showing potential for application in various areas [1]. Numerous parameter such as solution parameters (i.e., pH value, ionic strength and temperature) [2], operational parameters (i.e., dipping time and rinsing time) [3, 4] and polymer parameters (i.e., molecular weight and concentration) [5] are affecting the assembly growth and morphology of LbL thin film. Most naturally occurring polymer in the world is cellulose, which represents approximately 1.5×10^{12} tons yearly. In the past for many years, cellulose and its derivatives are widely used in many fields such as textile, pharmaceuticals, and foods, utilizing only very small portion. Therefore, there is a strategic necessity for the large-scale use of cellulose in an effective and green way, as petroleum resources are progressively exhausted [6, 7]. Due to difficulty in solubility of cellulose and organic solvent for cellulose are too strong to form inter-polymer complex, cellulose cannot be LbL assembled. But the cellulose can be modified to fit LbL assembly technique. Cellulose nanocrystal (CNC) is negatively charged and therefore it can be combined with a serial of positively charged polymers to prepare thin film via LbL assembly [8]. Formerly we investigated the effects of solution parameters on QC/CMC thin-film growth and morphology. It has been demonstrated that, the QC/CMC thin-film growth can be controlled by the pH value, ionic strength and temperature. In the neutral pH region or pH value less than 2.0, it is difficult for QC and CMC to be LbL assembled. The LbL assembly of QC and CMC is sensitive to ionic strength. As the ionic strength increases, the film growth is gradually restricted. Increasing the temperature accelerates the thickness growth of the films, but the film becomes rough and the transparency decreases [9]. The main focus of this work is to explore how the operational parameters influence the assembly growth of (CMC) and (QC) thin film.

Experimental Section

Materials



carboxymethyl cellulose
(CMC)



quaternized cellulose
(QC)

Figure1. Chemical Structure of CMC and QC [9].

Quaternized cellulose (QC) (M_w = 200,000-300,000, DS = 1.0) was delivered by Yan Cheng Xin Yuen Chemical Co. Ltd. Carboxymethyl cellulose (CMC, the viscosity of 2.0 wt. % water solution is ~ 550 mPa·s at pH = 6.15) was purchased from Sino Pharm Chemical Reagent. Hydrogen peroxide (H_2O_2) was obtained from Sino Pharm Chemical Reagent. Sulfuric acid (98 wt. %) and sodium hydroxide (NaOH) was acquired from Shanghai Ling Feng Chemical Reagent, and hydrochloric acid (HCl, 36.5 wt. %) was taken from Ping Hu chemical. All chemical were used as received.

Thin Film Preparation

The LbL assembly was conducted with an automatic dipping machine (Kejing Auto Instrument, Shenyang). The machine alternatively immersed the substrate into 1mg/ml QC solution and CMC solution for 4 minutes with an interval of 1 min each (three-times-rinsing) (pH = 4). The expression (QC/CMC) n, means the thin film was fabricated from QC and CMC through n dipping cycle. Films were deposited on silicon and quartz substrate, which were rigorously cleaned bevor used. The substrates were dipped in piranha solution (H2SO4/H2O2, 7:3 v/v) for 30 min (caution: this solution is extremely corrosive), followed by rinsing with deionized water for several times, then finally dried by stream of pure nitrogen gas.

Characterization

The films deposited on silicon wafer were characterized with Nicolet 8700 FT-IR spectrometer and blank silicon wafer was used to set background. The thickness of the thin film was determined with the method of optical reflectometry (λ range 200-1100 nm) [10]. The optical instrument NanoCalc-XR (Ocean Optics, Germany) was used to measure the near normal reflection spectroscopy of the thin film deposited on silicon wafer, and the film thickness was calculated based on the refection spectrum.

Results and discussion

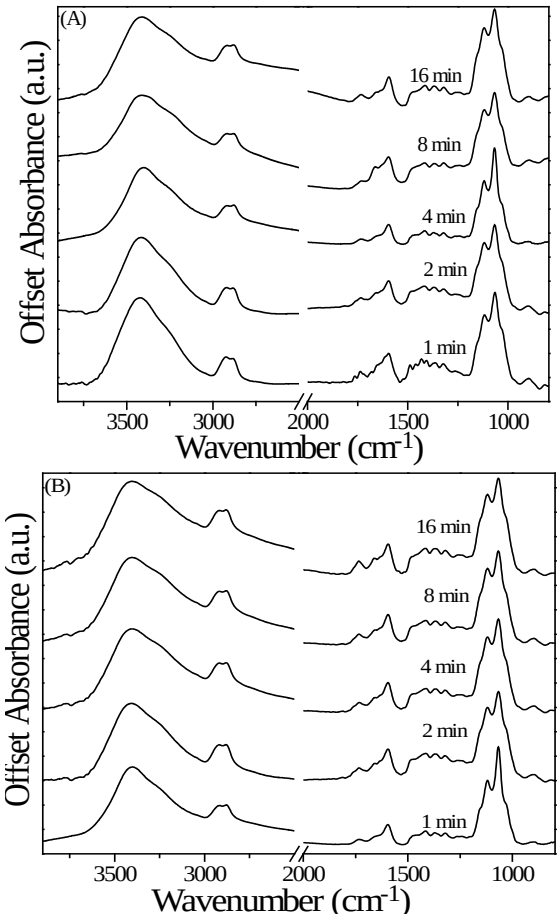


Figure2. The FT-IR spectra of $(QC/CMC)_{30}$ films prepared at pH 4: (A) different dipping time (B) different rinsing time.

QC and CMC were deposited on silicon substrate at different dipping and rinsing time. The FT-IR spectra of the films prepared at different dipping and rinsing time are shown in Fig. 2. FT-IR spectra indicate that at different dipping and rinsing time and pH 4 QC and CMC are successfully transferred to the silicon substrate.

Reflection spectra were applied to determine the thickness of QC/CMC thin films at different dipping and rising time the reflection spectra of the $(QC/CMC)_{30}$ thin films deposited on silicon are shown in Fig. Oscillation in spectrum area is due to optical interference of thin film, which is namely called Fabry-Perót fringes. With the help of these Fabry-Perót fringes, thickness of the thin film can be calculated by the following equation [10]:

$$d = \frac{m\lambda_k \lambda_{k+m}}{2n(\lambda_k + \lambda_{k+m})} \tag{1}$$

where d is the film thickness; n is the effective refractive index of the film; λ_k and λ_{k+m} are the peak positions of the kth and $(k + m)^{th}$ interference in the spectrum; and m is the difference in level between the two peaks. The thicknesses of the thin films prepared at different dipping and rinsing time are calculated based on Equation (1) and additional confirmed by data fitting using the software of NanoCalc-10n.

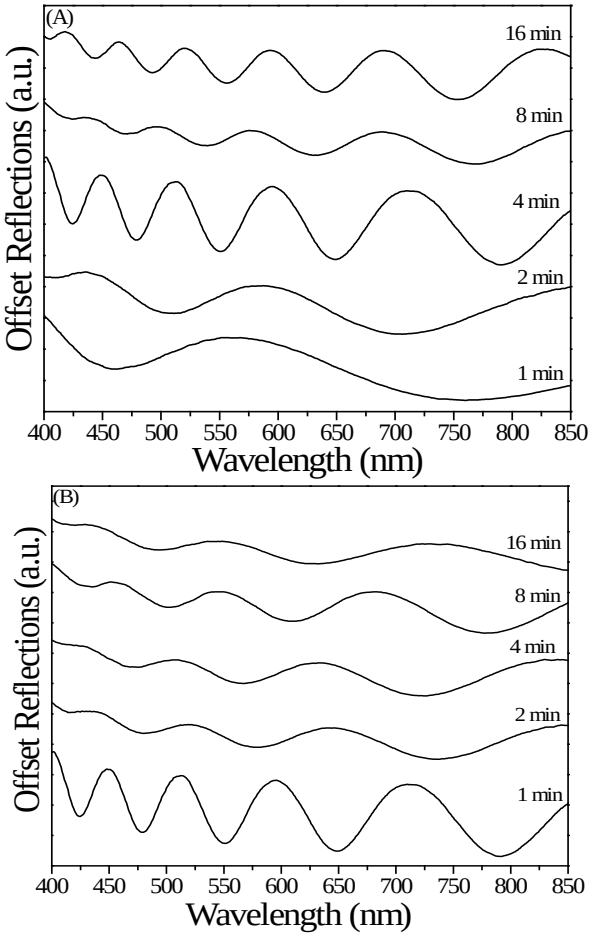


Figure3. The reflection spectra of $(QC/CMC)_{30}$ films prepared at pH 4: (A) different dipping time (B) different rinsing time.

The deposition of each polyelectrolyte takes place in two stages. First, the polyion chains attract electrostatically to the charged adsorption sites by a small number of ions that lasts a few second. Secondly, the remaining adsorption sites should be filled after adjustment and penetration of the polyelectrolyte chains between the sites already filled. This stage takes a few minutes to 20 minutes. As illustrated in literature [11] adsorption mainly occurs during the first 2 minutes after exposure of the substrate to the polyelectrolyte solution. Changing the dipping time changes the time available for the electrolyte to arrange them and ionically bond to the surface. Due to an increase in the number of the molecules on the surface and an increase of the dipping time, a thicker layer will be formed [12].

On the other hand, due to the long contact time in the dipping process, the polyelectrolyte chains have more time to diffuse into the formerly adsorbed layers in order to form complexes, to rearrange. Dipped LbL films are generated with adsorption over much longer periods, on the time scale of diffusion; polyelectrolyte chains in the bulk solution must diffuse through the solution into the positively charged surface. This relatively long diffusion time allows many of the polyelectrolyte chains that reach the surface to rearrange in an effort to reach thermodynamic equilibrium. Although such dipped films do not generally reach a true equilibrium state due to strong electrostatic charge interactions that pin chains to the surface, the longer dipping time does allow for more polyelectrolyte rearrangement on the surface and in the film [13].

Rinsing step is typically employed between polyelectrolyte dipping. The rinsing step serves to prevent contamination of the dipping solutions by removing excess and weakly held polyelectrolyte chains. Hoogeveen et al. have demonstrated the effect of rinsing time on thin films fabricated from polyvinlyimidazole (PVI) and poly (acrylic acid) (PAA). They concluded that increase in rinsing time results in the adsorption of more polyelectrolyte. Authors refers that more rinsing time

removes some loosely bound polymer and further help in rearrangement of the uppermost layer, providing a stabilizing effect on the growing film. However increasing of rinsing time leads to decrease of the film thickness [4].

Previously, we demonstrated that the interfacial complexation of QC and CMC originates from electrostatic interaction and hydration. When the electrostatic interaction become stronger, it can overcome the hydration effect, the QC and CMC can be LbL assembled. But when the hydration degree is strong, the QC and CMC cannot be LbL assembled. Therefore, with increasing the rinsing time the hydration becomes strong and the migration of polyelectrolyte chain from thin film to solution will occur, leading to decrease in the thickness of the fabricated thin film.

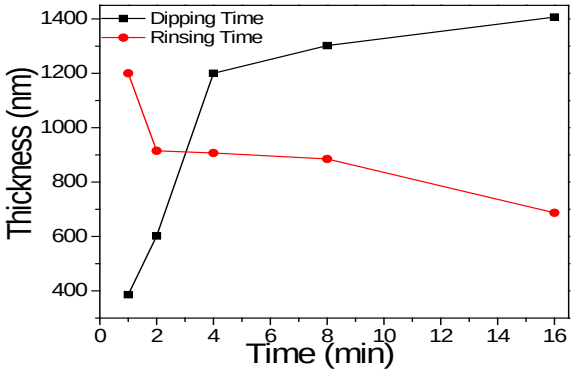


Figure 4. Thickness of the $(QC/CMC)_{30}$ thin films prepared at dipping and rinsing time.

Figure 4 shows the thickness of the QC/CMC thin films were deposited on silicon substrate and prepared at different dipping and rinsing time. Increasing of dipping time should have a large effect on film thickness, while increasing of rinsing time lead to decrease in thickness of the thin film.

Conclusions

In summary, thin film growth fabricated from QC and CMC can be controlled by the operational parameters. As rinsing time increases, the film growth is gradually restricted. We are also able to demonstrate that increasing the dipping time is help to achieve the maximum film thickness. The increase in dipping time also allow the inter diffusion of polyelectrolyte into the film.

Acknowledgment

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