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Interfacial Complexation Behavior of Anionic and Cationic Cellulose Derivatives

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Abstract

The oppositely charged cellulose derivatives, quaternized cellulose (QC) and carboxymethyl cellulose (CMC), were alternatively deposited on silicon or quartz substrates by interfacial complexation, i.e. layer-by-layer (LbL) assembly, to prepare the thin films. The factors of pH value, ionic strength and temperature on the thin film growth and morphology were investigated. The main chains of QC and CMC, composed by glucose rings, are hydrophilic and rigid, and hence QC and CMC show different assembly behavior compared with synthetic vinyl polyelectrolytes such as polystyrene sulfonate (PSS) and poly (diallyldimethyl-ammonium) (PDDA). As the pH value increases, in the region from pH 3 to pH 5 QC and CMC can be LbL assembled to prepare the thin film, in the neutron pH region QC and CMC are very hard to assemble, and when pH value is higher than 10, QC and CMC can be deposited again to fabricate the thin film. The LbL assembly of QC and CMC is sensitive to ionic strength. Adding 0.1 M NaCl into the assembling solution, the thin film growth tremendously decreases. Increasing temperature accelerates the thickness growth of the film.

Key Words: polymer complex, layer-by-layer assembly, cationic cellulose, anionic cellulose

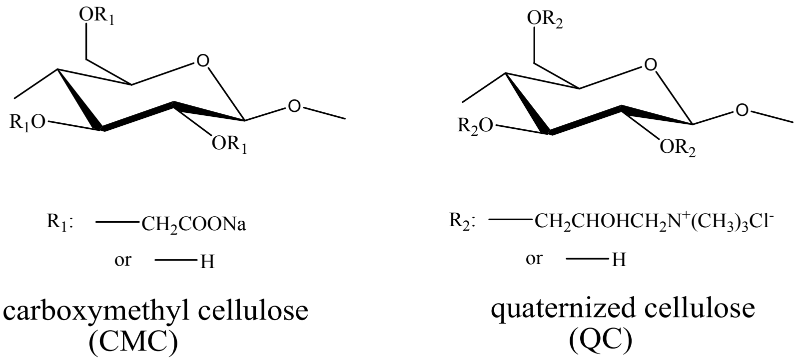
Introduction

Cellulose is the most abundant naturally occurring polymer around the world, and the yearly production of cellulose is estimated to be more than 1.5 trillion tons on earth. For a long time, cellulose and its derivatives have been widely used for textile and paper industry, pharmaceuticals, and foods, but only a small part of cellulose in nature has been utilized. It has strategic meaning for large-scaly using cellulose with an efficient and green way, as petroleum resource is gradually exhausted. [1-6]

Besides the traditional areas, the cellulosic polymers present many new applications in recent years, such as piezoelectric, [7-9] gene-carrier, [10] anti-reflection, [11] and anti-fogging. [12] Layer-by-layer (LbL) assembly, developed by Decher *et al.* in 1990s, has been proved to a simple but effective way to prepare thin films, coatings, or microcapsules with fine-tuned structures and components, showing potentials in various areas. [13-16] However, pure cellulose cannot be LbL assembled. The solvents for cellulose, including NMMO, DMA/LiCl, trifluoroacetic acid/chlorinated alkanes, urea/NaOH, ferric sodium tartrate, Cadoxen, Cuam, and Cuen, are too strong to form inter-polymer complex. But the cellulose can be modified to fit LbL assembly technique. Cranston and Gray reviewed the research work on LbL assembly containing cellulosic components, such as cellulose nanocrystals (CNC) and cellulose derivatives. [17]

CNC can be extracted from the bulk cellulose pulp by selective hydrolysis. The bulk cellulose pulp is composed by amorphous and crystalline region. The amorphous region of cellulose has quicker hydrolysis rate than crystalline region. [18-20] Through the acidic hydrolysis, the surface of CNC is negatively charged and hence CNC can be combined with a serial of positively charged polymers to fabricate thin film by LbL assembly. [21-26] Carboxymethyl cellulose (CMC) is a negative-charged derivative of cellulose and it has been paired with various cationic polyelectrolytes, such as PDDA, [27, 28] PAH, [29, 30] PEI and chitosan. [31, 32] The cationic cellulose derivative, quarternized hydroxyethylcellulose ethoxylate (HECE), was reported to be LbL assembled with CMC to prepare the thin film.[33] Hu *et al.* prepared the LbL assembled film of quarternized HECE and alginate and investigated the pH dependent behavior of electroactive myoglobin loading.[34] Besides electrostatic interaction, the neutral cellulose derivatives, such as cellulose ethers, were LbL deposited with poly(carboxylic acid) to prepare thin film basing on hydrogen bonding.[35, 36]

In this work we study LbL assembly of cellulosic polyelectrolytes, CMC and quaternized cellulose (QC), to prepare thin film, and investigate the effects of pH value, ionic strength and temperature on the thin film growth. The cellulosic polyelectrolytes have stiff and hydrophilic main chain, different to the synthetic polyelectrolyte, such as PAH and PDDA. The thickness growth of the CMC/QC film exhibits different dependence on ionic strength and pH value compared with the synthetic polyelectrolyte pairs.



Scheme 1 Chemical structures of CMC and QC

Experimental Section

Materials

Carboxymethyl cellulose (CMC, the viscosity of 2.0 wt. % water solution is ~ 550 mPa·s at pH = 6.15) was bought from Sino Pharm Chemical Reagent. Cationic cellulose (QC) (M_w = 200,000-300,000, DS = 1.0) was provided by Yan Cheng Xin Yuen Chemical Co. Ltd. Hydrogen peroxide (H_2O_2) was purchased from Sino Pharm Chemical Reagent. Sulfuric acid (98 wt. %) and sodium hydroxide (NaOH) were from

Shanghai Ling Feng Chemical Reagent, and hydrochloric acid (HCl, 36.5 wt. %) was from Ping Hu chemical.

Thin Film Preparation

The thin films were deposited on the substrates of quartz slides or silicon wafers. The substrates were cut into the desired dimension (1.2 cm × 4.5 cm), and were cleaned by immersing into *piranha* solution (H_2SO_4/H_2O_2, v/v, 7:3) for 1 h, followed by thorough rinsing with DI water and drying with nitrogen flow. The LbL assembly was conducted with an automatic dipping machine (Kejing Auto Instrument, Shenyang). The machine can be programmed to immerse the substrate into different solutions for different time. The substrate was alternatively dipped into the QC solution and the CMC solution for 4 min with the interval of three-times-rinsing (1 min each). The film is symbolized as $(QC/CMC)_{n,}$ and the subscript *n* means the thin film prepared through *n* assembling cycles. The CMC solution and the QC solution are both at the concentration of 0.1 wt. %. The pH values of the assembling solution and the rinsing solution were adjusted with HCl and NaOH under the monitoring of pH meter (SevenMulti, Mettler Toledo). The ionic strength of the assembling solution was adjusted by adding NaCl. The temperature was controlled by water bath.

Characterization

Quartz is UV-visible transparent and the thin film deposited on quartz substrate was measured by UV-visible spectrometer (Shimadzu UV-2550) directly. The films deposited on silicon wafer were characterized with Nicolet 8700 FT-IR spectrometer and blank silicon wafer was used as background.

The AFM images of the thin films deposited on silicon wafer were got from on an Agilent 5500 instruments under tapping mode. Commercial silicon probes (model TESP-100) with a typical resonant frequency of approximately 300 kHz and spring constant 40 N/m were used. Root-mean-squared (RMS) roughness of the QC/CMC thin film was determined by analyzing the AFM image (5 μm ×5 μm).

The quartz crystal microbalance (QCM) and chips were from Suzhou Institute of Nano-Tech and Nano-Bionics. QCM chips were modified by 5 mM

3-Mercaptopropionic acid solution in ethanol. The modified dry chip was mounted in the flow-through modules to establish a reference zero baseline. The resonance frequencies were monitored at the third overtone number. The QC solution and the CMC solution were alternatively pumped through the chips. During the switching of the assembling solution, the solvent flow (5 μL/min) was sent for several minutes to rinse the chamber.

The thickness of the thin film was determined with the method of optical reflectometry (λ range 200-1100 nm).[37] When light beams are reflected from the interfaces of film-air and substrate-film, there is phase difference and hence the superposition of amplitudes leads to different refection intensities at different wavelength. 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 calculated the film thickness based on the refection spectrum.

Results and discussion

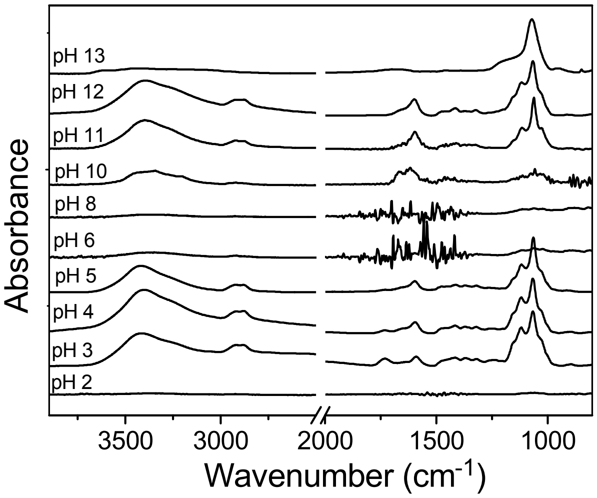


Figure 1 The FT-IR spectra of the $(QC/CMC)_{30}$ thin films prepared at different pH values (for clarity the spectra were intentionally overlaid).

Effect of pH value

The QC and CMC are deposited on silicon substrate at different pH values. The FT-IR spectra of the films prepared at different pH values were shown in the Figure 1. At pH 2 or less than pH 2, we could not observe the IR signal of the cellulosic component. In the neutral region, such as at pH 6 and pH 8, the IR signal of organic component is too weak to observe. At pH 13, we did not observed the absorbance signal from the cellulosic component and just from Si-O vibration, due to the silicon substrate was eroded by hydroxide. But, in the pH regions from 3 to 5 or from 10 to 12, there are strong IR absorbance of QC and CMC. The IR spectra demonstrated that the regions from pH 3 to pH 5 and from pH 10 to pH 12 are favorable for QC and CMC depositing on the silicon substrate to prepare the thin film.

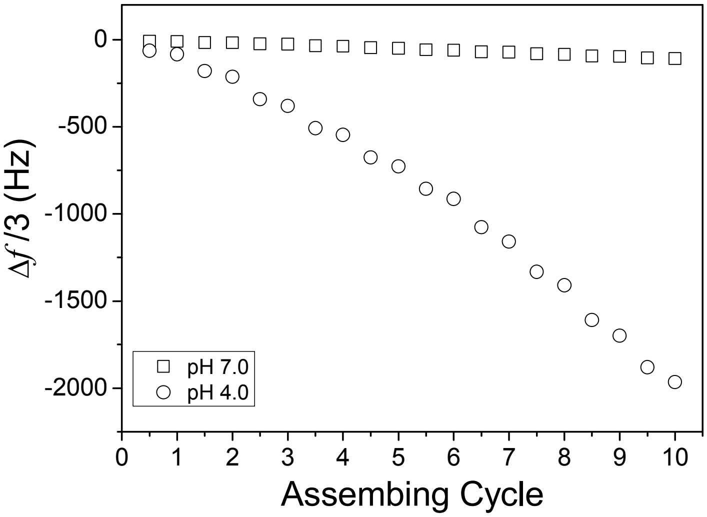


Figure 2 The frequency shift of the QC/CMC film as a function of assembling cycle. (Integrate number with 0.5 means QC is deposited at the outer layer)

Quartz crystal microbalance (QCM) was applied to monitor the QC/CMC film growth in-situ. When AC voltage is applied, the piezoelectric quartz crystal oscillates. The resonance frequency (*f*) of the crystal depends on the total oscillating mass. The frequency decrease (*Δf*) is proportional to the mass change, which was described by Sauerbrey equation: [38]

$$\Delta m = -C\frac{\Delta f}{n} \quad (1)$$

where Δm is the mass increment, C is the constant of the resonant chip and n is the overtone number. The frequency change as function of the assembly cycle was shown in Figure 2. When the QC and CMC were deposited at pH 4.0, the frequency exhibited big decreasing, whereas at pH 7.0, the frequency only showed small decreasing. According to Sauerbrey equation, at pH 4.0 the QC/CMC film growth is very fast while at pH 7.0 the film growth is extremely slow, which is corresponding to the result in Figure 1. Calculating with Sauerbrey equation (C =17.7 ng Hz^{-1} cm^{-2} and n = 3), the stable mass growth at pH 4.0 is 4.781 μg/cm^2 per assembling cycle. However, at pH 7.0, the mass growth is only 0.205μg/cm^2 per assembling cycle.

The reflection spectra were applied to characterize the QC/CMC thin film. The reflection spectra of the $(\mathrm{QC/CMC})_{30}$ thin films deposited on silicon are exhibited in Figure 3. The thin film prepared at pH 4 or pH 12, shows strong oscillations in the reflection spectrum. At pH 3 or pH 5, the thin film also exhibits oscillations, but is weak compared with the film prepared with at pH 4 or pH 12. At pH 11, the film shows trend to appear oscillation.

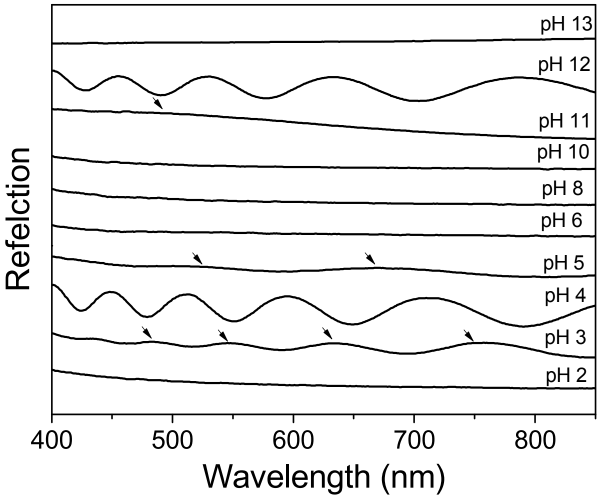


Figure 3 Reflection spectra of the $(\mathrm{QC/CMC})_{30}$ thin films deposited on silicon substrate at different pH values (for clarity the spectra were intentionally overlaid).

The oscillation in the spectrum is due to the optical interference of the thin film. If the thin film meets three requirements: (1) there is an obvious refractive index contrast between thin film and substrate, (2) the film thickness gets to the level of wavelength of light source, and (3) the film is very smooth, the optical interference phenomenon will present, as the oscillations on the spectrum in Figure 3. These oscillations in the spectrum are called the Fabry-Perót fringes. Utilizing the Fabry-Perót fringes on the spectra, we can calculate the thickness of the film with the equation as below: [39]

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

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 of the level between these two peaks. Equation (2) indicates that the peaks of Fabry-Perót fringes are determined by the optical thickness of the thin film (production of the physical thickness and refractive index of the thin film). The thin film is made from the cellulosic polymers and the refractive index of the thin film is closed to be 1.50. The thicknesses of the thin films prepared at different pH values are calculated based on Equation (2), and further confirmed by data fitting using the software of NanoCalc-10n. The thickness of the thin films prepared at different pH values were shown in Figure 4. pH 4 and pH 12 are two optimal pH conditions to prepare the thin film. The thin film $(QC/CMC)_{30}$ fabricated at pH 4 and pH 12 is 1220 nm and 1060 nm, and the average film growth per assembling cycle is 40.6 nm and 35.3 nm, respectively. QC and CMC both have rigid main chains, and the worm-like mode was applied to describe chain conformation. The film thickness growth per assembling cycle cannot estimate by the statistic size of polyelectrolytes. Generally, LbL assembly does not form well-defined lamellae structure. [13] The exponential mode is popular for LbL assembled polyelectrolytes thin film. *In-* and *out-diffusion* mechanism was applied to interpret exponential growth of LbL assembly. [40] The thickness growth per LbL assembling cycle represents different ends of a continuous spectrum of diffusion mobility. [41]

FT-IR spectra indicates that at pH 3, 4, 5, 10, 11 and 12, QC and CMC are successfully transferred to the silicon substrate, but only at pH 4 and at pH 12 the thin films exhibit strong optical interference. The thin film is made from cellulose derivatives and the refractive index of the thin film is about 1.50. The substrate is silicon and the refractive index of silicon is about 3.87. There exists an obvious refractive index contrast between the thin film and the substrate. If the film does not have optical interfere, the reason could be that the film does not meet thickness requirement or the thin film is too rough. If the thin film is thinner than 200 nm, it will be difficult to observe the apparent oscillation in the visible spectrum. If the thin meet the thickness requirement but the thin film is very rough, the light scattering will suppress the optical interference.

For the ideal smooth thin film, the amplitude of the Fabry-Perót fringes is determined by the refractive index of the thin film and the refractive index of the substrate. But in the real case, the thin film will exhibit roughness to some extent. As the roughness of the thin film increased, the light scattering effect will strengthen and the amplitude of Fabry-Perót fringes will become weak. As shown in Figure 3, the film prepared at pH 3 or pH 5 exhibits the very weak Fabry-Perót fringes compared with the film produced at pH 4, indicating that the pH 4 film is smoother than that the pH 3 film and the pH 5 film. It is very hard to find a proper physical mode to calculate the roughness size of the thin film basing on the reflection spectra data. But there is a simple way to describe the roughness degree of the thin film. Compared with the ideal smooth thin film, the percentage of light that loses from reflection beam direction can demonstrate the roughness of the thin film, and this value is defined as the roughness index. Through the data fitting procedure, the NanoCalc-XR software can give the roughness index of the thin films prepared at different pH values, as shown in Figure 5. At the pH 3 or the pH 5, the roughness index is higher than 70 % and hence the amplitude of Fabry-Perót fringes is very weak. At pH 4 and pH 12, the roughness index is simulated to be 21 % and 40 %, respectively.

The AFM was further applied to characterize the film roughness. The AFM images of thin films prepared at pH 4 and 12 were shown Figure 6. LbL assembly is an interfacial complexation process. CMC and QC form polymer complex at the interface, there is no crystallization involved in LbL assembly. Root mean square (RMS) roughness is 3.9 nm and 12.2 nm respectively, which is corresponding to the roughness index data in Figure 5.

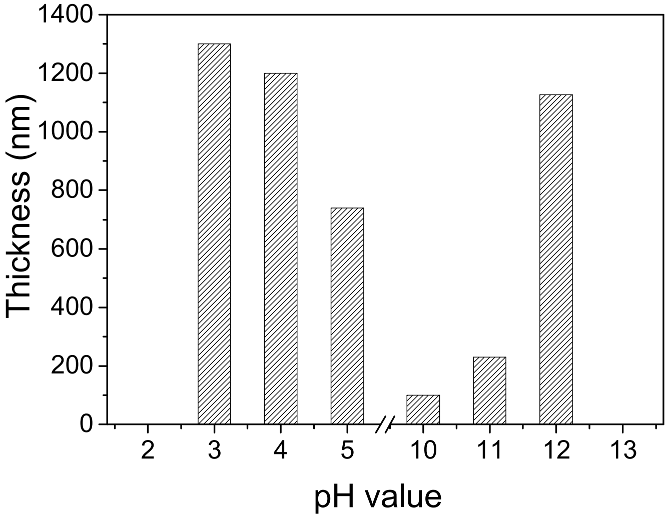


Figure 4 The thickness of the $(QC/CMC)_{30}$ thin films prepared at different pH values (room temperature).

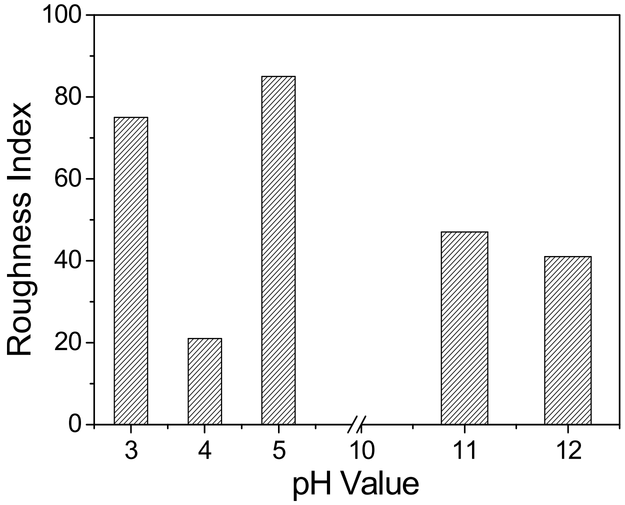


Figure 5 Roughness of the thin films prepared at different pH values.

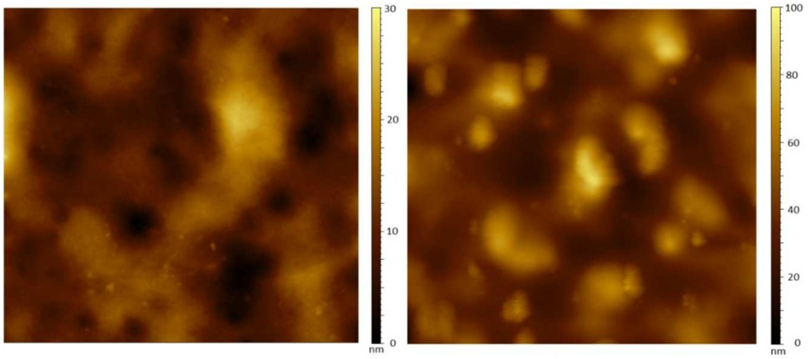


Figure 6 AFM (5 μm ×5 μm) images of the (QC/CMC)$_{30}$ thin films prepared at pH 4 (left) and pH 12 (right).

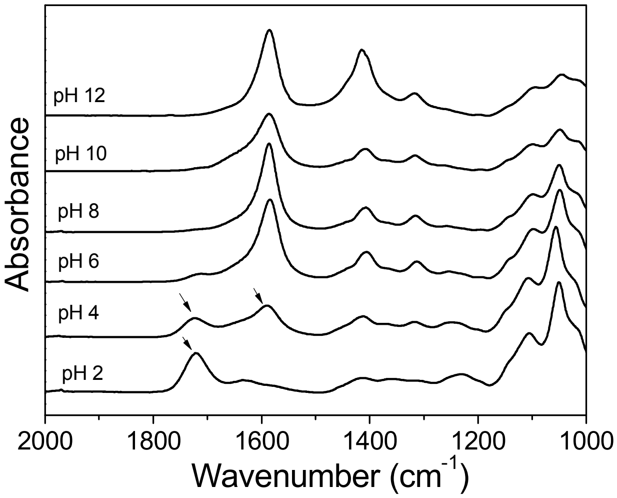


Figure 7 FT-IR spectra of CMC samples prepared from different pH value state.

QC is considered as a strong polyelectrolyte, while CMC is a weak polyelectrolyte. The charge density of QC can be considered not change when the pH value of the solution changes. However, as the pH value in the solution decreases, the ionization degree of CMC will become low and the charge density in CMC chain will correspondingly decrease. The charge density of CMC affects its interaction with QC. The FT-IR spectra were applied to determine the ionization degree of CMC. The CMC solutions at different pH values were frozen-dried, and then mixed with KBr powder and pressed into the standard discs for FT-IR characterization. The C=O stretching of COOH is located at 1730 cm^{-1}, however the asymmetric vibration of COO^{-} is located at 1585 cm^{-1} (Figure 7). The ionization degree was calculated with absorbance intensity at 1730 and 1585 cm^{-1}.[42, 43]

$$\alpha = \frac{\nu_{1585}}{\nu_{1730} + \nu_{1585}} \times 100\% \tag{3}$$

At pH 2.0, the ionization degree of CMC was estimated as 14 %. At pH 6.0 the ionization degree of CMC is more than 90 %. When the pH value higher than 8.0, the CMC is considered to be 100 % ionization. Compared with the synthetic polycarboxylic acid, such as poly(acrylic acid) (PAA), CMC is easy to ionize. At pH

2, the ionization of PAA is almost restricted while CMC shows 14 % ionization degree. PAA is vinyl polymer and its main chain is hydrophobic. But the main chain of CMC is hydrophilic. The main chain of CMC is composed by glucose rings and has high level hydration compared with PAA.

As the ionization degree of CMC increased, the electrostatic interaction between CMC and QC would be strengthen, which is favorable for the complexation and the LbL assembly of QC and CMC. But as pH value increases, the hydration of CMC and QC also change. It is considered that in the neutron pH value, QC and CMC show strongest hydration degree. The strong hydration will prevent the complexation of QC and CMC. The QC solution and the CMC solution were mixed at different pH values. In neutral pH regions, the mixed solution was clearer than that at pH 4 or pH 12, indicating that in the neutral pH region, QC and CMC have very weak complexation ability.

The pH effect on the interfacial complexation of QC and CMC is originated from electrostatic interaction and hydration. For example, at pH 8 CMC almost fully ionized but QC and CMC cannot LbL assembled to prepare the thin film due to strong hydration degree of QC and CMC. At pH 2 or less than pH 2, the ionization degree of CMC is relatively low and QC and CMC do not have enough electrostatic interaction to form the thin film. When the pH value of the solution increases from 2 to 5, the electrostatic interaction strengthens and can overcome the hydration effect, so QC and CMC can be LbL assembled. And at pH 4, there is a good balance between the cooperative electrostatic interaction and hydration and hence the high-quality QC/CMC thin film is fabricated. In the neutron pH value region the hydration becomes dominated and CMC and QC are hard to prepare the thin film. When the pH value is over 10, the hydration of QC and CMC will become weak and they can be LbL assembled to prepare the thin film again.

When pH value is elevated to 13, QC and CMC cannot be assembled on silicon substrate, but they can successfully deposit on quartz substrate. It was found that at pH 13 or higher than 13, silicon is eroded by hydroxide group. Strong base can also erode the quartz, but quartz has stronger resistance to hydroxide than silicon.

Ionic strength effect

Ionic strength is an important factor that will affect the thickness growth of the synthetic polyelectrolyte complex thin film, such as PSS/PDDA and PSS/PAH. [44-46] The presence of salt in these polyelectrolyte solutions greatly affects the chain conformation. Without additional salt in the solutions, the same type charges within a polyelectrolyte chain repel each other, such that the chain is fully extended. When intentionally adding salt into the solutions, the charge repulsion among the polyelectrolyte chain will be screened and the chains will present as random coils. When the polymer chains are transferred from the solution to the interface, the chain conformation in the solution will affect the polymer stacking and the thickness growth. It has been reported that the films produced under high salt concentrations are thicker and have a higher surface roughness. [44-46]

However, the ionic strength dependence on the thickness growth of QC/CMC is different to the synthetic polyelectrolyte complex thin films. As shown in Figure 8, as the ionic strengthen increased, the thin film growth become slow. With adding 0.5 M NaCl, the thin film growth is almost restricted.

QC and CMC are different to PSS, PDDA or PAH. The main chains of the PSS, PDDA and PAH are pure carbon chain, which are hydrophobic. However, the main chain of QC and CMC are β-linked glucoses, which are hydrophilic. And the main chains of QC and CMC are much stiffer than the main chain of PSS, PDDA or PAH. Adding salt into the solutions mainly weakens the electrostatic interaction between QC and CMC, but imposes a small effect on the polymer chain conformation compared with PSS, PDDA or PAH.

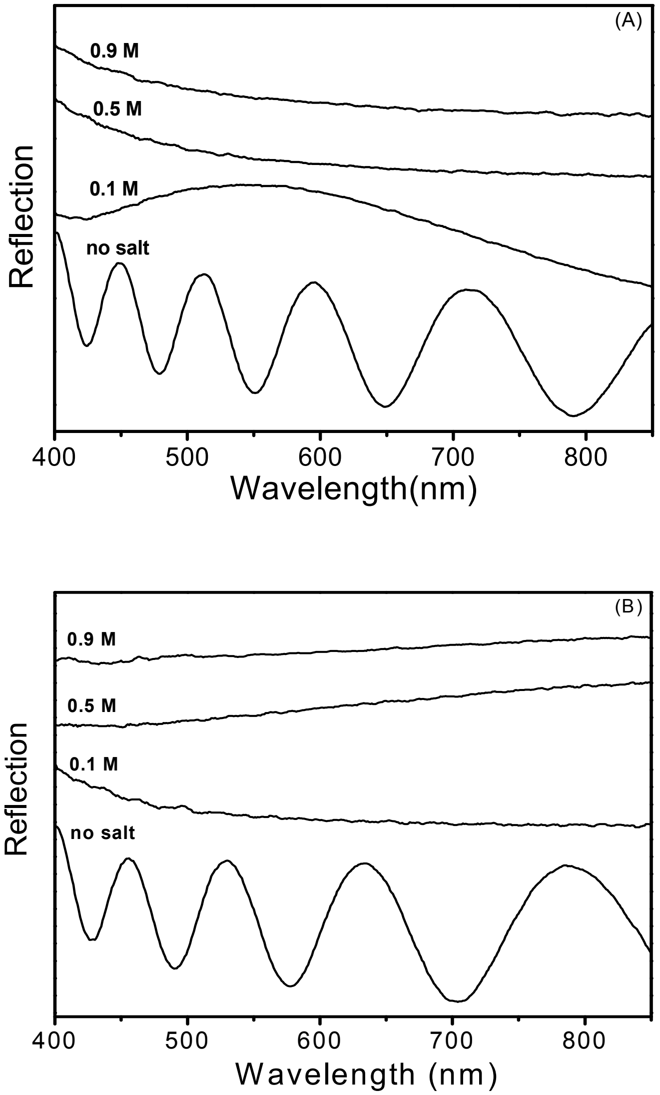


Figure 8 The reflection spectra of the $(QC/CMC)_{30}$ films prepared with adding different content sodium chloride: (A) pH 4.0; (B) pH 12.0.

To further demonstrate the salt effect on the complexation behavior of QC and CMC, the QC solution and the CMC solution were mixed at a 1:1 molar ratio with different ionic strength. The turbidity of the mixed solution was measured with UV-visible spectrometer, as shown in Figure 9. Without adding salt, the solution is cloudy. When the salt concentration is higher than 0.1 M, the mixed solution becomes clear. The resultant clear solution demonstrated the solid-like polymer complex is hard to form, suggesting that the thin film basing on interfacial complexation in the presence of salt would be prohibited.[47]

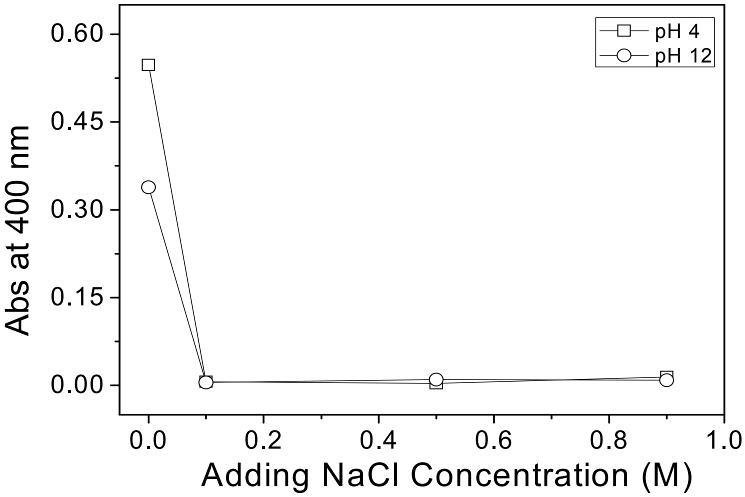


Figure 9 Turbidity of the CMC and QC mixed solutions of adding NaCl with different concentration.

Temperature effect

Temperature plays a positive role on the film growth. As shown in Figure 10, the thicker thin film is produced when temperature increases. The temperature effect on the synthetic polyelectrolyte complex thin films or the hydrogen-bonded thin films has been investigated. [48, 49] For the strong polyelectrolyte pair PSS/PDDA, as temperature elevated, the film thickness growth accelerates. [46] For the hydrogen-bonded complex thin film PVPON/PAA, the film thickness growth also become quick as the temperature increased. [49] The polymer complexation process is mainly driven by the entropy. [14] It means that the entropy is positive and it can compensate the unfavorable enthalpy. Increasing temperature will amplify the effect of the entropy and contribute for more negative free energy. So from thermodynamic aspect, increasing temperature is helpful to form the thin film.

From kinetic aspect, increasing temperature accelerates the diffusion. During the LbL assembly process, there are two kinds of diffusion. One is that polymer diffuses from the solution to the interface, and the other is polymer diffusion inside the film. Generally, LbL assembly does not produce the stratified structure and there exists interpenetration to some degree. For the weak polyelectrolyte film or the hydrogen-bonded film, there exists high-level interpenetration, which indicates the stronger polymer diffusion inside the film. Picart *et al.* put forward *in*- and *out*-diffusion mode to demonstrate the mechanism of the exponential growth mode of the PLL/HA film. [40] The polymer diffusion inside the polymer complex thin film should be a common phenomenon. Temperature effect on the QC/CMC film growth should also have contribution from the acceleration of the diffusion inside the film.

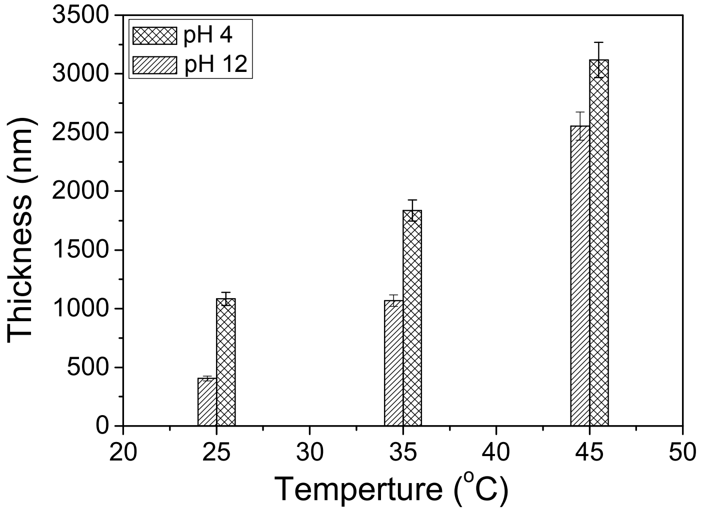


Figure 10 Thickness of the $(QC/CMC)_{30}$ thin films prepared at different temperature.

Conclusions

The LbL assembly behavior of cellulosic polyelectrolytes is different to the synthetic vinyl polyelectrolyte pairs. Due to the hydrophilic main chain, QC and CMC have high level of hydration degree. The complexation and LbL assembly of QC and CMC are affected by hydration and electrostatic attraction. The QC/CMC thin film growth can be controlled by the pH value, ionic strength and temperature. As temperature elevated, the film growth becomes quick. As the ionic strength increased, the film growth is gradually restricted. In the neutron pH region or pH value less than 2.0, QC and CMC are hard to be LbL assembled.

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Interfacial Complexation Behavior of Anionic and Cationic Cellulose Derivatives

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