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In situ Investigation on Layer-by-Layer Deposition of Polyelectrolytes by Quartz Crystal Microbalance

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The effect of salt concentration on layer-by-layer deposition of poly(sodium 4-styrene sulfonate) (PSSS)/poly(vinylbenzyl trimethylammonium chloride) (PVTC) was investigated by use of quartz crystal microbalance with dissipation (QCM-D). The changes in frequency and dissipation demonstrate that the addition of NaCl leads the thickness of PSSS/PVTC multilayer to increase. The deposition of PSSS/PVTC is dominated by surface charge overcompensation level at lower salt concentrations. However, it is mainly determined by the interpenetration of polyelectrolytes at a higher salt concentration, as reflected in the oscillation of dissipation change.

Key words: Polyelectrolyte, Layer-by-layer deposition, Quartz crystal microbalance

I. INTRODUCTION

The sequential layer-by-layer (LBL) self-assembly of oppositely charged polyelectrolytes on a solid substrate results in a polyelectrolyte multilayer (PEM) [1,2]. In the past decade, the LBL assembling technique has proven to be a versatile method for surface modification [3-7]. This approach has found applications in photodiodes [8], optical devices [9], chemical sensors [10], nonlinear optics [11], and drug delivery [12]. It has been reported that the PEM thickness increases with the concentration of the added salt in terms of the charge overcompensation level and the polyelectrolyte conformations of the outmost layer [13]. However, Schlenoff and Dubas revealed that the charge overcompensation level (ϕ) was almost independent of salt concentration [14,15], so they proposed that the thickness increment was primarily controlled by the charge penetration length (l_{cp}). So far, the salt effect on LBL deposition remains unclear.

The quartz crystal microbalance (QCM) has been used to investigate the growth of multilayers [16-19]. However, the conventional QCM can only provide limited information about the mass change or frequency shift. Recently, QCM with dissipation (QCM-D) has been introduced, which can detect the changes in both mass and structure of a film [20-30]. In this work, by use of QCM-D, we investigated the LBL deposition of poly(sodium 4-styrene sulfonate) (PSSS)/poly(vinylbenzyl trimethylammonium chloride) (PVTC) as a function of salt concentrations in real time in order to understand the mechanism for multilayer growth.

II. EXPERIMENTS

PSSS and PVTC were synthesized by reversible addition fragmentation chain transfer polymerization (RAFT) in water [31]. The number-average molecular weights (M_n) and the polydispersity indexes (M_w/M_n) of the samples were measured by size exclusion chromatography (Shodex OHPak SB-806M HQ) using monodisperse poly(ethylene glycol) as the calibration standard. The mobile phase consisted of Milli-Q water, 0.5 mol/L Na₂SO₄, 0.03 mol/L NaN₃ at a flow rate of 1.0 mL/min. For PSSS, $M_n \approx 28$ kg/mol, $M_w/M_n = 1.04$. For PVTC, $M_n \approx 1.8$ kg/mol, $M_w/M_n = 1.07$.

QCM-D with an AT-cut crystal was from Q-sense AB. The fundamental resonant frequency of the crystal was 5 MHz. The crystal was mounted in a fluid cell with one side exposed to the solution [32]. The constant (C) of the crystal was 17.7 ng/cm²Hz. The measurable frequency shift was within ± 1 Hz in aqueous medium. The effects of surface roughness were neglected because the crystals were polished with the RMS roughness less than 3 nm [33].

A quartz crystal is excited to oscillate in the thickness shear mode at its fundamental resonant frequency (f_0) when a RF voltage near the resonant frequency is applied across the electrodes. A small layer added to the electrodes would induce a decrease in resonant frequency (Δf) which is proportional to the mass (Δm) of the layer. In vacuum or air, if the added layer is rigid, evenly distributed and much thinner than the crystal, Δf is related to Δm and the overtone number ($n = 1, 3, 5, \dots$) by the Sauerbrey equation [34],

$$\Delta m = -\frac{\rho_q l_q}{f_0 n} \Delta f \quad (1)$$

where f_0 is the fundamental frequency, ρ_q and l_q are the specific density and thickness of the quartz crystal,

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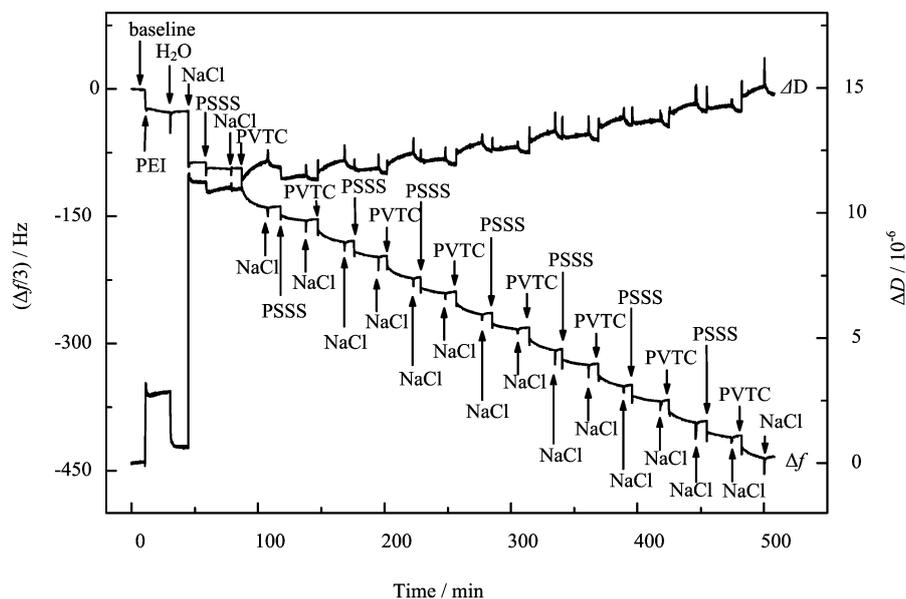


FIG. 1 Changes in frequency (Δf) and dissipation (ΔD) of LBL deposition of PSSS/PVTC at 30 °C, where NaCl concentration is 1.0 mol/L and the overtone number is 3.

respectively. The dissipation factor is defined by

$$\Delta D = \frac{E_{\text{dissipated}}}{2\pi E_{\text{stored}}} \quad (2)$$

where $E_{\text{dissipated}}$ is the energy dissipated during one oscillation and E_{stored} is the energy stored in the oscillating system. ΔD is measured based on the fact that the voltage over the crystal decays exponentially as a damped sinusoidal when the driving power of a piezoelectric oscillator is switched off [32]. By switching the driving voltage on and off periodically, we can simultaneously obtain a series of the changes of the resonant frequency and the dissipation factor.

Since the Sauerbrey equation is not valid for a viscoelastic polymer layer in a Newtonian liquid, the thickness of the layer was fit by theoretical representations based on a Voigt model with the Q-tools software from Q-sense AB [35]. Considering that the bulk solution is dilute, its density (ρ_l) and viscosity (η_l) are taken to be those of water, that is, $\rho_l \approx 1000 \text{ kg/m}^3$ and $\eta_l \approx 1 \text{ mPa}\cdot\text{s}$, respectively. The density (ρ_f) of the adsorbed layer is estimated to be $\sim 1000 \text{ kg/m}^3$ as a fixed value in the fitting.

The gold-coated resonator was cleaned using Piranha solution composed of one part H_2O_2 and three parts H_2SO_4 , rinsed with Milli-Q water, and blown dry with a stream of nitrogen gas. A measurement of LBL deposition was initiated by switching the liquid exposed to the resonator from Milli-Q water to a poly(ethyleneimine) (PEI, $M_w \approx 25 \text{ kg/mol}$) solution with a concentration of 1 mg/mL. PEI is allowed to adsorb onto the resonator surface for ~ 20 min before rinsing with water to ensure a uniform positive charged coating so that the effects of the substrate on the layer growth are minimized

[36]. After water was replaced with pure NaCl solution, 0.1 g/L PSSS and PVTC were alternately introduced for 20 min with pure NaCl solution rinsing in between. Δf and ΔD values from the fundamental were usually noisy because of insufficient energy trapping and thus discarded [37].

III. RESULTS AND DISCUSSION

Figure 1 shows the changes in frequency (Δf) and dissipation (ΔD) for the LBL deposition of PSSS/PVTC at 30 °C, where the NaCl concentration is 1.0 mol/L. Before the other polyelectrolyte was introduced each time, a pure NaCl solution was added to keep the two polyelectrolytes from forming complexes in solution. The decrease in Δf and increase in ΔD clearly indicate that the polyelectrolytes gradually deposit onto the resonator surface.

Figure 2 shows NaCl concentration dependence of $-\Delta f$ of PSSS/PVTC as a function of layer number at 30 °C, where the odd and even layer numbers correspond to the deposition of PSSS and PVTC, respectively. It shows that $-\Delta f$ increases linearly with layer number, indicating a gradual deposition of the polyelectrolytes. For the same layer number, $-\Delta f$ increases with NaCl concentration, indicating that the thickness of PEM increases with salt concentration.

Figure 3 shows NaCl concentration dependence of ΔD of PSSS/PVTC as a function of layer number at 30 °C, where the odd and even layer numbers correspond to the deposition of PSSS and PVTC, respectively. Obviously, ΔD also increases with the layer

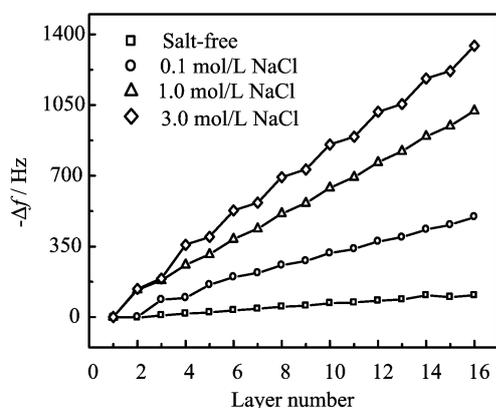


FIG. 2 Change in frequency (Δf) of PSSS/PVTC as a function of layer number at 30 °C with different NaCl concentrations, where the overtone number is 3. The odd and even layer numbers correspond to the deposition of PSSS and PVTC, respectively.

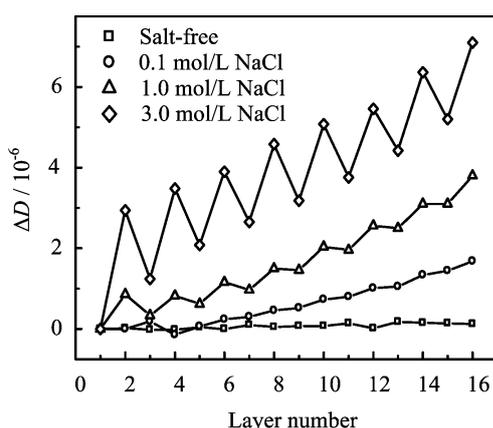


FIG. 3 Change in dissipation (ΔD) of PSSS/PVTC as a function of layer number at 30 °C with different NaCl concentrations, where the overtone number is 3. The odd and even layer numbers correspond to the deposition of PSSS and PVTC, respectively.

number, further indicating the gradual deposition of polyelectrolytes. At the same time, an obvious oscillation can be observed in the change of ΔD at higher NaCl concentrations. Note that no “oscillation” occurs when NaCl concentration is low.

It is known that the dissipation factor of a film relates to its structure. A dense or rigid layer has a small dissipation factor, whereas a looser or more flexible structure has a larger one [35]. The oscillation actually reflects the interpenetration of polyelectrolytes. For a certain PSSS outer layer, when PVTC is introduced, due to the interaction between some negative charges on PSSS chains and the positive charges on PVTC chains, a swollen PVTC layer is formed on PSSS surface. Thus, ΔD increases. However, the subsequently introduced PSSS chains would penetrate into PVTC layer, leading to the complexation between PSSS and PVTC chains.

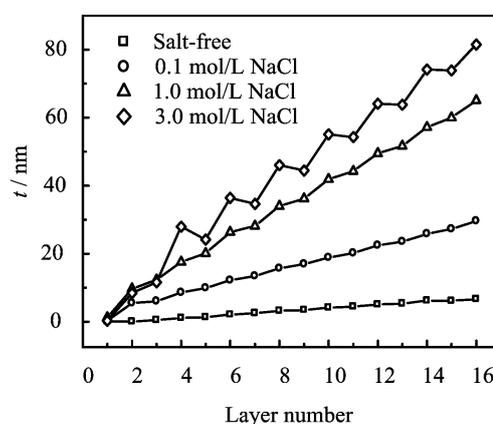


FIG. 4 The hydrodynamic thickness (t) of the PSSS/PVTC multilayer at 30 °C with different NaCl concentration as a function of layer number fit by Voigt model. The odd and even layer numbers correspond to the deposition of PSSS and PVTC, respectively.

As a result, the layer becomes denser, as reflected in the drop in ΔD . At the same time, the surface charge changes from positive to negative, making the subsequent adsorption of PVTC chains on the surface possible.

In this work, for the same layer number, $-\Delta f$ increases with salt concentration at the lower salt concentrations, whereas ΔD does not exhibit obvious oscillation. This is because polyelectrolyte chains form more loops or tails at the outmost layer as the salt concentration increases [13]. The loops and tails can extend into the solution and carry excessive charges, leading the charge overcompensation level to increase. Thus, more polyelectrolyte chains are adsorbed so that the thickness of the multilayer increases. Note that the charge overcompensation only works on the loops or tails, so the interpenetration occurs to a limited depth. That is why no obvious ΔD oscillation is observed.

Due to the electrostatic repulsive interactions between like charges, the charge overcompensation attains a critical level at a certain salt concentration. Further increasing the salt concentration leads the oppositely charged polyelectrolyte chains to diffuse into the interior of the multilayer. In other words, the charge penetration length increases. As a result, more polyelectrolytes in solution are trapped in the multilayer, leading to a thicker PEM. Meanwhile, ΔD exhibits obvious oscillations, further indicating the interpenetration increases. We obtained similar results at 20 and 25 °C (data not shown). Figure 4 shows the hydrodynamic thickness (t) of PSSS/PVTC multilayer at different NaCl concentrations as a function of layer number fit by Voigt model [35]. Clearly, the thickness changes at higher NaCl concentrations also indicate the oscillation. The agreement between the experimental and fitted results further indicates the chain interpenetration.

IV. CONCLUSION

In this work, the effect of salt concentration on layer-by-layer deposition of PSSS/PVTC was investigated by use of quartz crystal microbalance with dissipation (QCM-D). The investigations can lead to the following conclusion. The LBL deposition is dominated by the surface charge overcompensation level at lower NaCl concentrations but by the interpenetration between neighboring layers at higher NaCl concentrations.

V. ACKNOWLEDGMENT

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