



# Salt effects on the structural tailoring of layer-by-layer assembled polyelectrolyte complexes and salt-containing polyelectrolyte films



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## ABSTRACT

Structural tailoring of layer-by-layer (LbL) assembled polymeric films prepared by alternate deposition of polyelectrolyte-polyelectrolyte complexes (PECs) and oppositely charged salt-containing polyelectrolyte was systematically studied as a function of NaCl concentration in the polyelectrolyte solution. At pH 9.3, positively charged poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) complexes (denoted as PAH-PAA9.3) could be LbL assembled with poly(sodium 4-styrenesulfonate) (PSS) to produce PSS/PAH-PAA9.3 films even with high NaCl concentration in PSS solution. Moreover, both the thickness and structure of the films were strongly depended on the concentration of NaCl in PSS solution. The salt in PSS solution can influence the conformation of PSS chains, but cannot interfere with the interaction and structure of PAH-PAA complexes deposited on substrates. Therefore, at relatively high NaCl concentration, a rough surface with hierarchical micro- and nanostructures can be obtained due to the coiled conformation and increased rigidity of PSS when they were LbL deposited with PAH-PAA complexes. By contrast, LbL deposition of flexible and extended PSS with PAH-PAA complexes at low NaCl concentration can produce a thin film with smooth structure. The present study is meaningful in deeply understanding the salt effect on the deposition behavior and structural tailoring of LbL assembled PECs and salt-containing polyelectrolyte films.

## 1. Introduction

Layer-by-layer (LbL) assembly, which involves alternate deposition of species with complementary chemical interactions, has become increasingly important for the ease, flexibility and versatility in fabrication of functional film materials conformal on diverse substrates [1–6]. Besides traditional electrostatic interaction, some non-electrostatic interactions such as hydrogen-bonds, coordination interactions, guest-host chemistry and so forth were also explored as the driving forces for LbL film fabrication in recent years [3–8]. Up to now, LbL assembly had found various applications in the fields such as superhydrophobic/superoleophobic surfaces [5,9–14], biosensors [2,15–17], drug/gene delivery systems [16–20], separation membranes [21,22], corrosion resistance films [23,24], self-healing coatings [5,24–26], anti-fogging and anti-frosting surfaces [26,27], energy storage and conversion [2,17,28–30], and so forth. As structure begets functions, the wide range of applications of LbL assembled films in diverse areas origin from the abundance and highly controllable structure of the LbL assembled films. Compared with other film preparation methods, LbL assembly is unique as the structure and properties of the LbL assembled

films including thickness, morphology, wettability, permeability, and swelling/shrinking behavior can be precisely controlled on micro- and nano-scaled [1–7]. Multiple means can be used to tailor the architecture and properties of LbL assembled films including varying the assembled conditions such as ion strength [31–35], pH [14,36,37], temperature [34,38,39] etc. of the building blocks, or by the post film treatment process [40–42]. Investigation of the structural tailoring of LbL assembled films is always a core issue of LbL assembly as it not only can endure the films with structure and functions, but can give a general rule to predict the construction of various functional film materials by LbL assembly technique.

Generally, building blocks that can adjust their structures and properties with external environment are ideal for LbL assembly as it enables more possibilities to achieve the structural tailoring of the films and therefore broaden the application range of LbL assembled films [5,14,25,42]. Recently, polyelectrolyte complexes (PECs), which are a class of supramolecular assemblies intertwined together mainly by electrostatic interaction between polycations and polyanions [5,43–45], have been widely used to fabricate LbL assembled films with new structures as well as functions [5,46–55]. Compared with

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uncomplexed polyelectrolyte, the PECs have abundance of composition and relatively large dimension, which facilitates the functional integration and rapid fabrication of LbL assembled film materials [5,48–54]. More importantly, the structures of PECs are diverse and can be flexibly controlled by changing parameters such as mixing ratio [5,50,51,56], solution pH [57–59], ionic strength [54,56,60–63], temperature [64,65], etc. [66], during or after PEC formation. These merits of PECs on one hand open up opportunities for the construction of functional films that are difficult or impossible to prepare by LbL deposition of uncomplexed polyelectrolytes, on the other hand realize the flexible structural tailoring of LbL assembled films [5,49–54]. The structural tailoring of LbL assembled films using PECs as building blocks is far more complicated than that of the films fabricated with uncomplexed polyelectrolyte because not only the structure of PECs themselves but the structure of LbL assembled films can be influenced by the parameters mentioned above [5]. Therefore, it is highly desired and necessary to systematically study the structural tailoring of LbL assembled films that are composed with PECs.

Among various influencing parameters, ionic strength has a great effect on both the structure of PECs and LbL assembled films fabricated using PECs as building blocks [5,54]. In our previous work, we have demonstrated that at pH 6.5, LbL assembly of salt-containing non-stoichiometric poly(allylamine hydrochloride) (PAH)-poly(acrylic acid) (PAA) complexes with oppositely charged polyelectrolyte poly(sodium 4-styrenesulfonate) (PSS) can directly fabricate a dewetting-induced porous polymeric films [54]. More importantly, the porous film structure can be finely tailored by NaCl concentration in PAH-PAA dispersions. However, in some cases, the structures of LbL assembled films composed of PECs and oppositely charged polyelectrolytes are impossible to be tuned by changing the ion strength of PEC dispersions. Because increasing the ion strength of PEC dispersions will induce the precipitation of PECs immediately, especially for the ones with relatively large dimensions. For these kinds of PECs, the structural tailoring of corresponded LbL assembled films could be realized by changing the ion strength of the polyelectrolyte solution that is used as the partner component to alternately deposit with PECs. In this paper, deposition behavior and corresponding structural tailoring of LbL assembled PECs and salt-containing polyelectrolyte films were systematically investigated. Different from porous film structure, LbL deposition of PAH-PAA complexes (pH 9.3) with oppositely charged salt-containing PSS (pH 9.3) could rapidly produce a rough and thick film with hierarchical structure under a nondrying LbL deposition process. Moreover, the film thickness and hierarchical structure could be well tailored by changing NaCl concentration in PSS solution. After chemical vapor deposition of a layer of fluoroalkylsilane, the films with hierarchical structure can be conveniently converted into hydrophobic surfaces with controlled surface wetting properties, which are also highly dependent on ion strength in PSS solution. As an extended investigation of our previous work, present work is meaningful for further deeply understanding structural tailoring of LbL deposited PEC films as a function of ion strength in polyelectrolyte solution.

## 2. Materials and methods

### 2.1. Materials

Poly(allylamine hydrochloride) (PAH,  $M_w$  ca. 56,000), poly(acrylic acid) (PAA,  $M_w$  ca. 1800), PSS ( $M_w$  ca. 70,000), and poly(diallyldimethylammonium chloride) (PDDA,  $M_w$  ca. 100,000–200,000) were purchased from Sigma-Aldrich. 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (POTS) was purchased from Degussa. Sodium chloride was analytical grade and was purchased from Beijing Chemical Reagents Company. All chemicals were used without further purification. Deionized water was used for the preparation of PECs and LbL assembled films.

### 2.2. Preparation of PAH-PAA9.3 complexes

PAH-PAA complexes were prepared by directly mixing of aqueous PAA (10 mg/mL, 30 mL) solution into aqueous PAH (1.1 mg/mL, 470 mL) solution under intense stirring. The ultimate concentrations of PAH and PAA in complex solution were 1.0 and 0.6 mg/mL, respectively, which correspond to a feed monomer molar ratio of 1:0.75 PAH/PAA. The pH of aqueous PAH-PAA dispersion was adjusted to 9.3 by diluted NaOH. In order to distinguish experimental conditions we used in our previous paper [55], here we use PAH-PAA9.3 to represent PAH-PAA complexes with their pH being 9.3. The as prepared PAH-PAA9.3 complexes were continuously stirred for another 2 h before being used for LbL film fabrication.

### 2.3. Film preparation

Silicon wafers were immersed in piranha solution (1:3 mixture of 30%  $H_2O_2$  and 98%  $H_2SO_4$ ) and heated until no bubbles were released. **Caution!** Piranha solution reacts violently with organic material and should be handled carefully. The cleaned quartz and silicon wafers were immersed in PDDA aqueous solution (1.0 mg/mL) for 20 min to obtain a cationic ammonium-terminated surface. The pH of the PSS solution was adjusted to 9.3 by 0.1 M NaOH. PSS (pH 9.3) with different NaCl concentration were alternatively deposited with positively charged PAH-PAA9.3 complexes to fabricate multilayered films of PSSm/PAH-PAA9.3 (where m refers to NaCl concentration in PSS solution).

PDDA modified silicon wafer was first immersed into an aqueous PSS solution (pH 9.3, 1 mg/mL with m M NaCl) for 20 min, rinsed with water (pH 9.3) three times for 1 min each time. The substrate was then transferred to an aqueous dispersion of PAH-PAA9.3 complexes for 20 min to obtain a layer of PAH-PAA9.3 complexes followed by rinsing with water (pH 9.3) three times for 1 min each. Unless otherwise stated, no drying steps were conducted during the coating deposition except at the end of coating fabrication. Multilayered films of (PSSm/PAH-PAA9.3) $_n$  (note: n represents the number of deposition cycles) can be fabricated by repeating these steps in a cyclic fashion by a programmable dipping machine.

### 2.4. Chemical vapor deposition of POTS

The substrate deposited with PSSm/PAH-PAA9.3 film was placed in a sealed vessel, on the bottom of which was dispensed a few drops of POTS. There was no direct contact between the substrate and the drops. The vessel was put in an oven at 120 °C for 2.5 h to enable the vapor of POTS to react with the –OH groups on the substrate surface. Finally, the substrate was taken out of the vessel and placed in an oven at 180 °C for another 1.5 h to volatilize the unreacted POTS molecules on the substrate.

### 2.5. Characterization

Multilayer film fabrication was conducted with Dipping Robot DR-3 (Riegler&Kirstein GmbH) at room temperature. Dynamic light scattering studies and  $\zeta$ -potential measurements were carried out on a Malvern Nano-ZS zetasizer at room temperature. The measurements were made at a scattering angle of  $\theta = 173^\circ$  at 25 °C using a He-Ne laser with a wavelength of 633 nm. Scanning electron microscopy (SEM) images were obtained on a XL30 ESEM FEG scanning electron microscope. The LbL-assembled films deposited on silicon wafers were cleaved for cross-sectional SEM images. All films were coated with a thin layer of gold (2 to 3 nm) prior to SEM imaging. Film thickness and root-mean-square (rms) roughness of LbL assembled coatings ( $500 \times 500 \mu m^2$ ) were measured with a Dektak 150 surface profiler using a 5  $\mu m$  stylus tip with a 3 mg stylus force. Atomic force microscopy (AFM) images were taken with a Nanoscope IIIa AFM Multimode (Digital Instruments, Santa Barbara, CA) under ambient conditions. AFM was operated in the

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