

## Temperature Effect on Layer-by-Layer Self-assembly of Linear Polyions and Silica Multilayers

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Alternate layer-by-layer self-assembly of linear polyions and colloidal silica at elevated temperatures has been investigated by QCM and SEM. A growth step at 90 °C for these multilayers was about 100–200% larger than the one at 20 °C.

Layer-by-layer (LbL) self-assembly of films containing oppositely charged polyions and nanoparticles is an effective and economic approach to deposit ultrathin organized films or to fabricate micro- and nanodevices.<sup>1–3</sup> For example, the films of six-layer silica 45 nm in diameter and poly(dimethyldiallyl ammonium chloride) were self-assembled to produce capacitor arrays on a standard 4-inch silicon wafer.<sup>4</sup> Optimization of the LbL assembly process is an important task to transfer this promising academic technique to industry. Varying deposition time, adjusting pH values of polyion solution, changing ionic strength, or using non-aqueous solvents were recognized as effective ways to optimize precise LbL coating of polyions and nanoparticles.<sup>5–13</sup> Temperature is another experimental parameter to control the growth rate of LbL self-assembled films.

Poly(dimethyldiallyl ammonium chloride) (PDDA) was assembled with sodium poly(styrenesulfonate) (PSS) (both 3 mg/ml aqueous solutions, pH 6.5; purchased from Sigma) on a quartz crystal microbalance (9 MHz QCM, USI-System, Japan) by dipping the QCM plate in the solution of polyions at 22 °C, 60 °C, and 90 °C. Frequency shift can be converted to layer thickness ( $L$ , nm) using an empirical formula  $L = -0.016 \Delta F$  for linear polyions and  $L = -0.022 \Delta F$  for silica/PDDA layers.<sup>5,6</sup>

Two types of colloidal silica (Nissan Kagaku, Japan), 45 nm and 300 nm in diameter, were assembled with PDDA at pH 9 at different temperatures. The self-assembly was performed at elevated temperatures as well as room temperature (22 °C). The frequency measurements for the film thickness were also implemented at room temperature. In a separate experiment, a bare QCM resonator was heated and tested. The frequency shift was very small, indicating that temperature effect on QCM itself can be neglected.

The assembly of PSS/PDDA multilayers at 60 °C and 90 °C showed much larger growth steps as compared with the assembly at room temperature (Figure 1). An average frequency shift ( $\Delta F$ ) for a PDDA layer taken from the fifth step to the tenth step was about 190 Hz corresponding to 3.0 nm at 22 °C, 400 Hz (6.4 nm) at 60 °C, and 430 Hz (6.9 nm) at 90 °C. For PSS the average step was 270 Hz (4.3 nm) at 22 °C, 700 Hz (11.2 nm) at 60 °C, and 900 Hz (14.4 nm) at 90 °C. Both linear polycation and polyanion layers have a similar tendency to increase thickness with temperature.

Figure 2 shows QCM monitoring for 45-nm silica nanoparticles assembled with PDDA at different temperatures. An analysis of PDDA growth steps gives an average frequency shift from 150 Hz (2.4 nm) at 22 °C to 480 Hz (7.8 nm) at 90 °C, close to the thickness of polyion layers in the assembly of linear PDDA

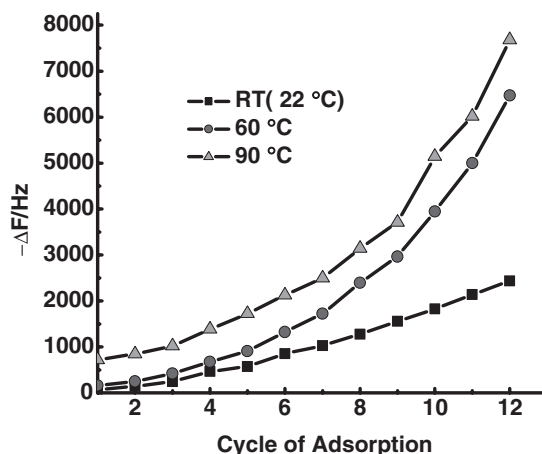


Figure 1. Frequency shift for PDDA(PSS/PDDA)<sub>2–12</sub> at different temperatures.

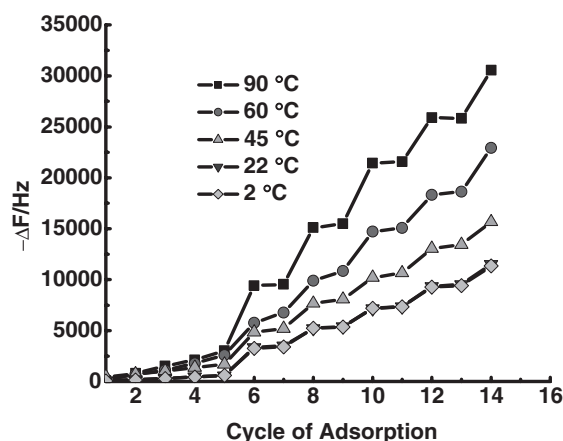
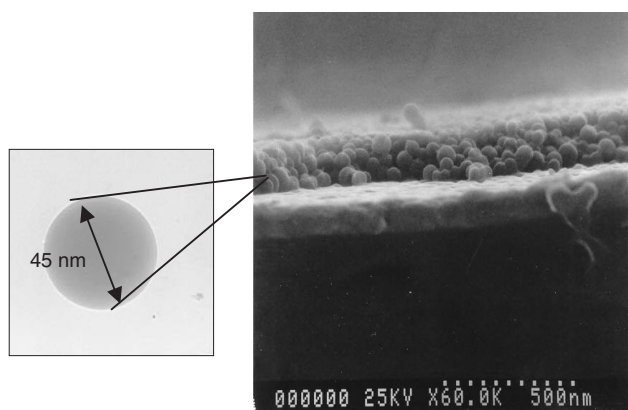


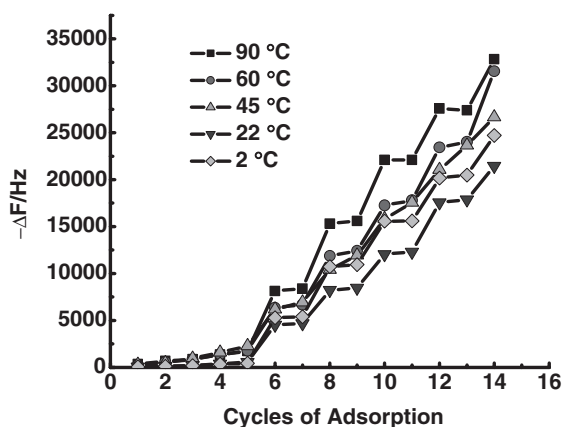
Figure 2. Frequency shift of PDDA(PSS/PDDA)<sub>2</sub> + (PDDA/45-nm silica)<sub>5–14</sub> at different temperatures.

and PSS. The thickness of the silica layer also increases with temperature. The average frequency shift corresponding to the silica deposition step was 2200 Hz (48 nm, about one monolayer) at 22 °C and 6000 Hz (132 nm, three monolayers in one adsorption cycle) at 90 °C. Figure 3 illustrates a SEM image of a closely packed film formed by the alternation of PDDA and 45-nm silica. The surface roughness of nanoparticle thin film prepared under different temperatures was inspected. Typically the roughness  $R_a$  is about 4 nm at 22 °C, about 4 nm at 60 °C, and about 6 nm at 90 °C. The experiments show that raising temperature has little effect on the roughness of multilayer films self-assembled with linear polyions and 45-nm silica nanoparticles.

Figure 4 shows a similar temperature effect for the self-assembly of 300-nm silica nanoparticles. The multilayer thick-



**Figure 3.** Cross-sectional SEM image of PDDA(PSS/PDDA)<sub>2</sub>+(45-nm silica/PDDA)<sub>4</sub> assembly on a silver electrode (Hitachi S-900 SEM, voltage 25 kV, the sample coated with Pt 2 nm thick).



**Figure 4.** Frequency shift of PDDA (PSS/PDDA)<sub>2</sub>+(PDDA/300-nm silica)<sub>5-14</sub> at different temperatures.

ness of (Silica/PDDA)<sub>5</sub> increases from 480 nm at 22 °C to 720 nm at 90 °C.

One of the approaches to analyze the above experimental results was that LbL self-assembly behavior could be explained by considering the temperature effect on pH values of the solution as described by the Arrhenius equation.<sup>14</sup> However, a possible pH shift corresponding to the investigated range of temperatures on  $\pm 1$  from pH 6.5 (i.e., within pH 5.5–7.5) will have little effect on the charge of such strong linear polyions as PDDA and PSS,

which are completely ionized at these pH values. A change in diffusion coefficients of the components could hardly explain the phenomena, because our adsorption time (10 min) is about 100 times longer than the diffusion limitation time needed to form a monolayer.<sup>3</sup> The Kinetics of the adsorption process connected with a density of initially anchored polyions to the charged surface is a more probable reason for the found dependences.

Therefore, a new phenomenon in layer-by-layer self-assembly of linear polyions and nanoparticles, 100–200% increase of growth step with temperatures, was found, and it has to be taken into account in the applications of LbL technique. The possible mechanism may involve the temperature effects of polymer conformation, dielectric constant of medium, electrostatic interaction, enthalpy/entropy balance in charge shielding, the surface coverage of polymers and the aggregation of polymers at greater temperatures due to dehydration.

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