

# CHEMPHYSICHEM

## Supporting Information

### **Growth Kinetics in Layer-by-Layer Assemblies of Organic Nanoparticles and Polyelectrolytes**

Maziar Mohammadi,<sup>[a]</sup> Ali Salehi,<sup>[b]</sup> Ryan J. Branch,<sup>[b]</sup> Lucas J. Cygan,<sup>[b]</sup> Cagri G. Besirli,<sup>[c]</sup> and Ronald G. Larson<sup>\*[a, b]</sup>

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## Supporting information

### 1. Effect of deposition time

Figure S1 depicts the effect of deposition time on the growth kinetics of a poly(ethyleneimine) (PEI)/polystyrene (PS) layer-by-layer (LbL) assembled film. PEI with a molecular weight (MW) of 70 kg/mol and 41 nm-sized negatively charged PS (PS-hereafter) nanoparticles were chosen for this experiment.

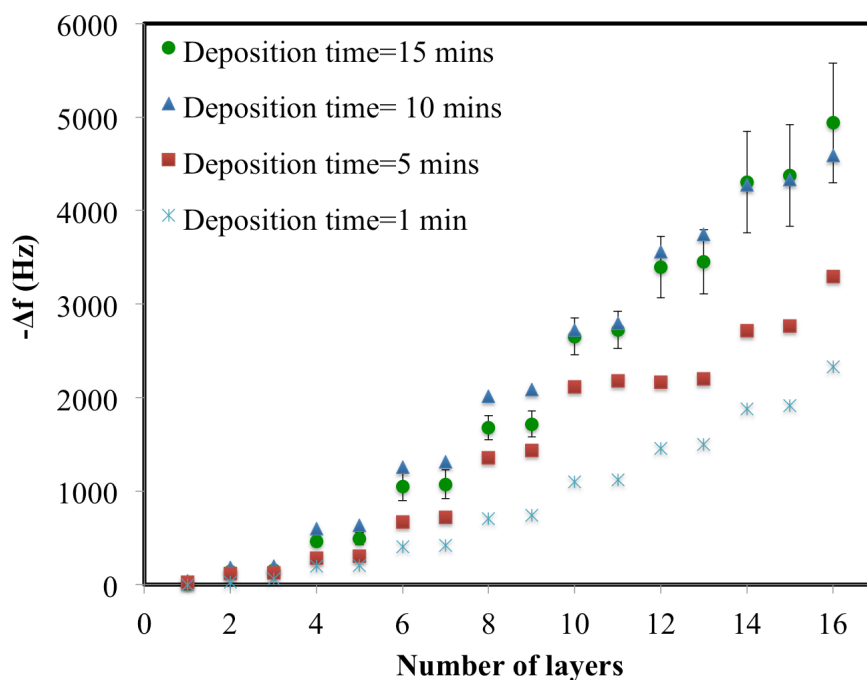


Fig. S1. The effect of deposition time on LbL growth of PEI/PS- composite.

As shown in Fig. S1, increasing the deposition time boosts the growth of PEI/PS-composites up to around 10 minutes deposition time. Upon increasing the deposition time up to this limit, polyelectrolytes (PEs) and nanoparticles (NPs) are evidently more diffused to the film. However, it seems that the growth of the film becomes saturated and does not vary much beyond a deposition time of 10 minutes. This trend was observed in other LbL film buildup studies as well.<sup>[1]</sup> Based on these observations, 15 minutes was allowed for deposition during each step of LbL growth with QCM (8 double layers) in our experiments. However, for growing thick LbL films (59 double layers), a deposition time of 10 minutes was considered to save time while maintaining considerable film growth.

## 2. Charge compensation factor

For the data shown in Fig. 2 of the manuscript, charge compensation factor defined by following equations is calculated and shown in Fig. S2 below.

$$\Gamma_i = \frac{\Delta m_i^{NP} \sigma^{NP}}{\Delta m_i^{PE} \sigma^{PE}} \quad (S1)$$

$$\sigma^{NP} = \frac{\# \text{ surface charges of NP}}{\text{Mass of NP}} \quad (S1-1)$$

$$\sigma^{PE} = \frac{f_{PE}}{\text{MW of monomer}} \quad (S1-2)$$

In Eq. (S1),  $\Gamma_i$  is the charge compensation factor calculated for each PE/NP double layer  $i$ ,  $\Delta m_i$  is the deposited mass for each NP or PE layer,  $\sigma$  is the surface charge per unit weight, and  $f_{PE}$  is linear charge density of PE bounded within [0,1] such that a fully charged PE corresponds to  $f_{PE} = 1$ . The MW of a PEI monomer is 43.07 g/mol. The number of charged functional groups on the NP surface is determined using the surface charge density reported by the manufacturer. Note that the PE layer goes down first followed by the PS layer. Hence, overcompensation of PE charge by the deposited PS layer would require that  $\Gamma_i > 1$ . If  $\Gamma_i < 1$ , the PE charge is undercompensated.

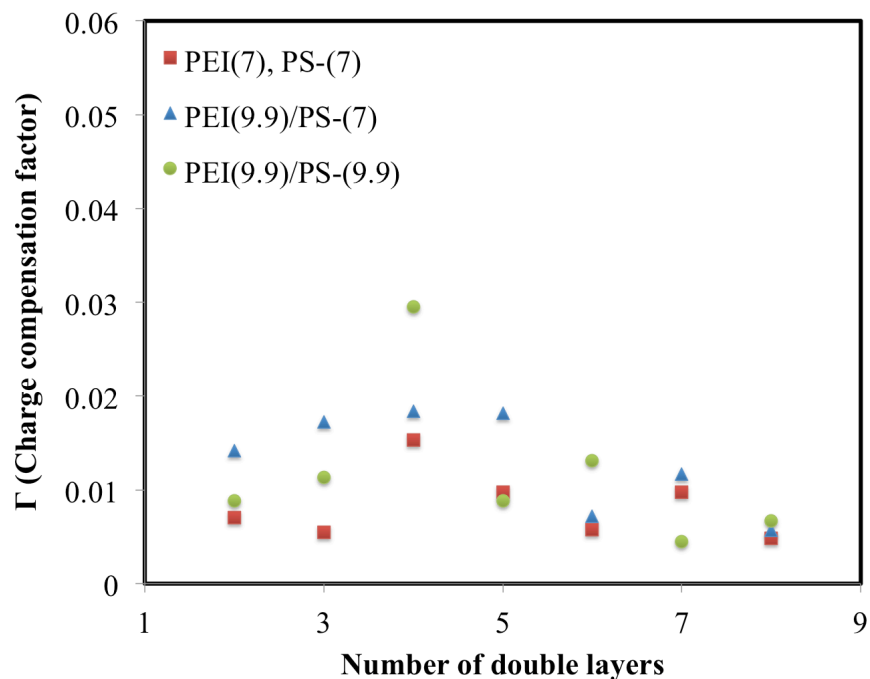


Fig. S2. Charge compensation factor for PEI/PS- composites grown with different pH values (pH of each deposition solution is shown in the parentheses in the legend). PEI with a MW of 70 kg/mol and 41 nm-sized PS- particles are used for this experiment.

Conspicuous in Fig. S2 is the very low charge compensation factor (on the order of 0.01) for PEI/PS- composites. We believe that NPs act as spacers and promote LbL growth despite not having a 1-to-1 charge compensation in the film.

In Fig. S2, the data for the first double layer is not shown, since the value for  $\Delta m_i$  of PE for the first double layer was very low and the resulting value of compensation factor became very large, placing it significantly outside the range of the charge compensation factors for the rest of data points.

### 3. Effect of pH drift

Figure S3 shows the effect of pH drift on LBL growth of a PEI/PS- composite. PEI with a MW of 750 kg/mol and 41 nm-sized PS- particles were used for this experiment. For one case the pH of PS- suspension and rinsing waters was monitored prior to each respective deposition, while for the case without pH monitoring, the pH value of the solutions and rinsing waters was set at the beginning of the experiment.

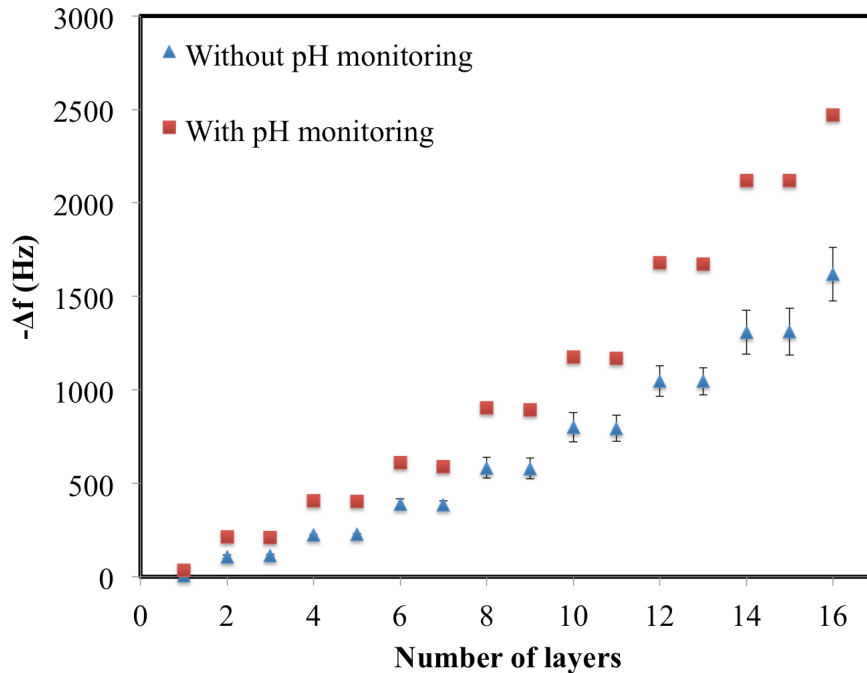


Fig. S3. Influence of pH drift on the PEI/PS- film buildup, PEI (odd numbered steps) and PS- (even numbered steps) are deposited at pH values of 9.9 and 7, respectively. No salt was added to either of the ingredient of the LbL film except for the ions introduced to the solutions by pH adjustment.

As shown in Fig. S3, by constantly monitoring and adjusting the pH, a boost in LbL growth is achieved. As mentioned in the text, when the pH difference between PEI and PS- deposition steps is increased, faster LbL growth occurs. Adjusting the pH value of deposition solutions during LbL assembly enables one to better maintain such a pH difference.

#### 4. Effect of nanoparticle concentration on the growth of PAA/PS+ composite

Figure S4 shows the role of concentration of positively charged PS (PS+ hereafter) NPs on the growth kinetics of poly(acrylic acid) (PAA hereafter)/PS+ multilayers.

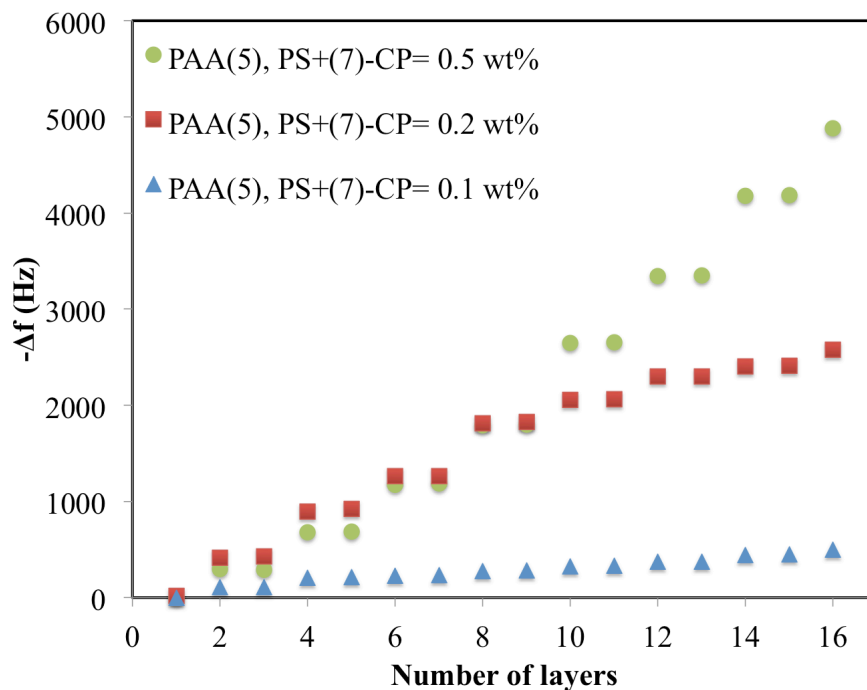


Fig. S4. The effect of PS+ concentration on LbL film buildup of PAA/PS+ composite. PAA with MW of 240 kg/mol and 100 nm-sized PS+ particles were employed. CP refers to the concentration of particles.

According to Fig. S4, increasing the PS+ concentration increases the film growth rate. The enhancement in the growth kinetics is more pronounced when the concentration is incremented from 0.1wt% to 0.2wt%. The rise in the number of NPs in the media presumably increases their availability near the solution-film interface and results in more adsorption into the film.

## 5. Effect of deposition pH on surface morphology of the LbL films

Figure S5 contrasts the surface morphology of two LbL films deposited at different pH conditions. For both cases PEI with a MW of 70 kg/mol and PS- particles with 41 nm size were used. Other than ions introduced to the solutions for pH adjustment, no salt ions were added to the deposition solutions.

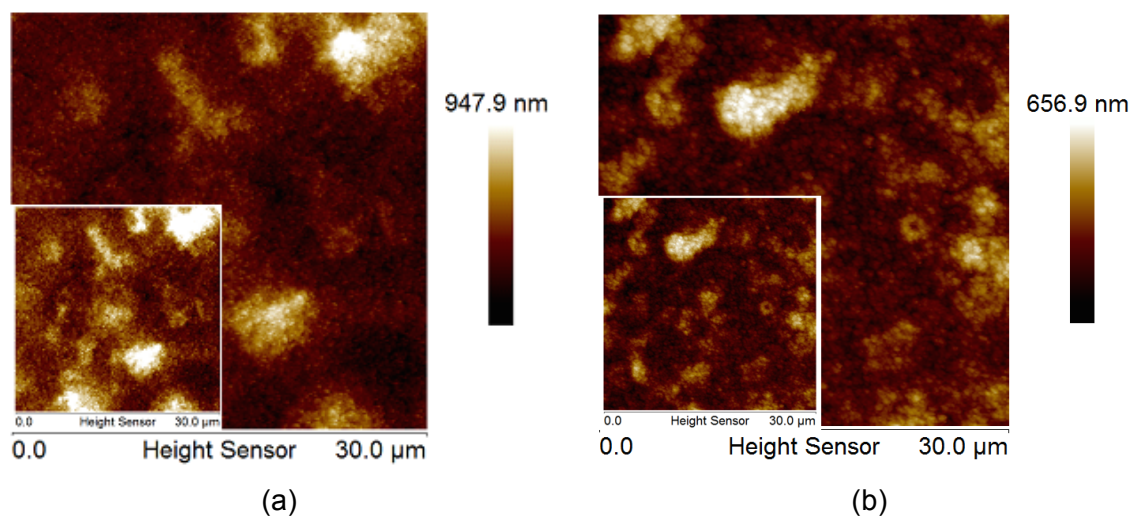


Fig. S5. Surface characteristics of LbL films composed of 8 bilayers of PEI with MW of 70 kg/mol and 41 nm sized PS- particles deposited at different pH values. No salt was added for the deposition of either of film ingredients. a) Film growth at pH amplified condition. PEI and PS- are deposited at pH values of 9.9 and 7, respectively. b) PEI and PS- are both deposited at pH value of 7. For the plots in the inset, maximum value of color bar is fixed to 700 nm.

As seen in Fig. S5, films deposited at pH-amplified condition have a larger absolute roughness. However, as mentioned in the manuscript, this film has a much faster growth rate. Comparing the two plots in Fig. S5 considering roughness to thickness ratio, one can understand that for a given film thickness, the film deposited in pH amplified condition has around 30 % less roughness value.

## 6. Film surface

Figure S6 shows surface features of a sample LbL film obtained by optical microscope of the AFM.

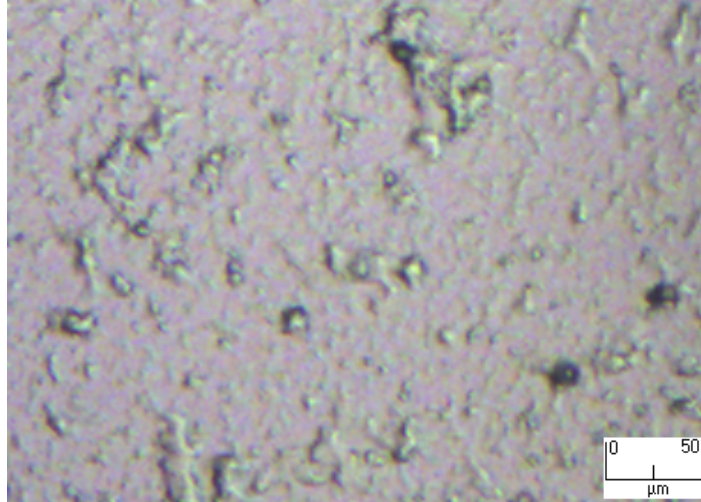


Fig. S6. An optical micrograph of the surface features of the LbL films. PEI with a MW of 70 kg/mol and PS- particle size of 41 nm were used, with six double layers deposited.

[1] M. Rahman, N. Taghavinia, *The European Physical Journal-Applied Physics* **2009**, 48, 10602.