

Supporting Information

Effects of applied voltage and solution pH in fabricating multilayers of weakly charged polyelectrolytes and nanoparticles

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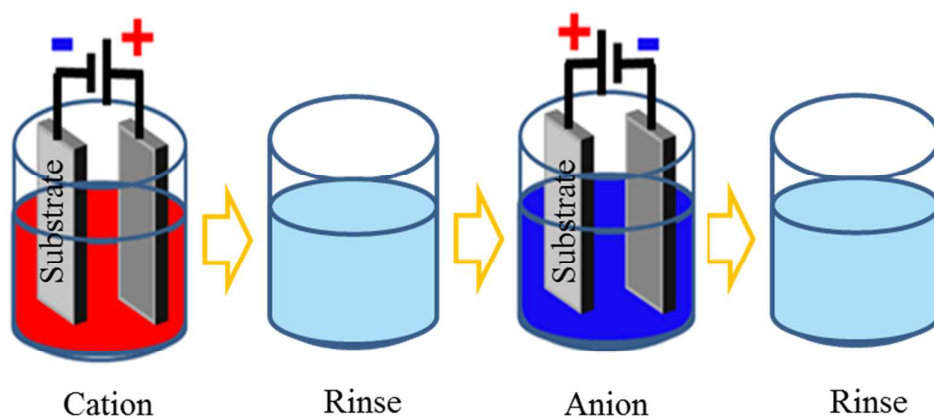
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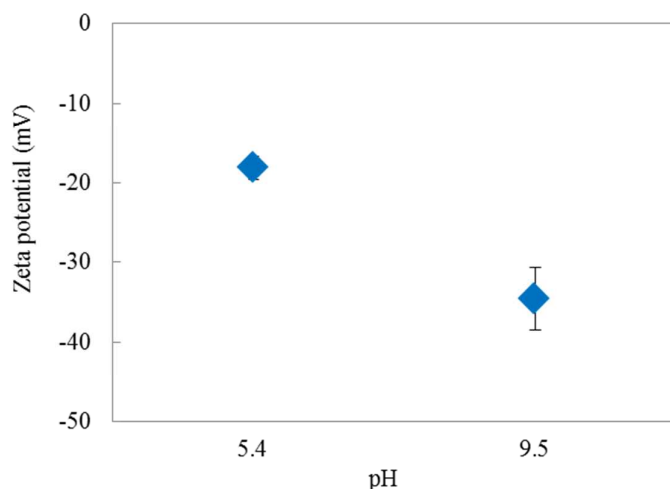
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We investigated the relationship between polymer chain conformation and the effects of applied voltage, in the LbL self-assembly of weakly charged PAH/PAA polyelectrolytes and SiO₂ nanoparticles. Solution pH values were varied, and PAH/PAA films and PAH/SiO₂ films were fabricated by LbL self-assembly under applied voltages. The experimental setup is shown in Fig. **SI Figure 1**. As shown in the figure, negative voltage was applied in the cation solution bath, and on the other hand, positive voltage was applied in the Anion bath.



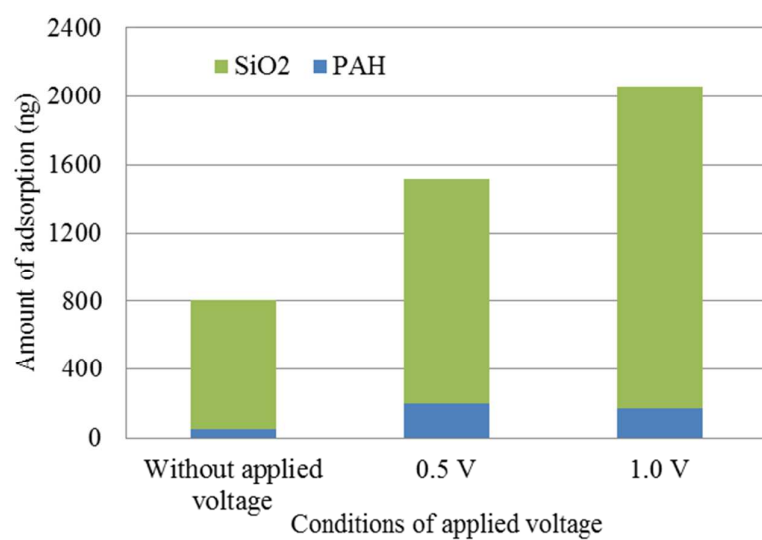
SI Figure 1. Experimental equipment used for fabrication of film under applied voltage.

There are a lot of Si-OH groups on the surface of SiO₂ nanoparticle. It is known that isoelectric point of SiO₂ solution is around pH 2.1.⁴³ When the pH of SiO₂ solution is higher than 2.1, the surface of nanoparticle is negatively charged. In fact, zeta potential of SiO₂ nanoparticles at pH 5.4 and 9.5 was measured, as shown in **SI Figure 2**. For the deposition of LBL films, SiO₂ nanoparticles at pH 5.4 and 9.5 were regarded as anion because the zeta potential at both pH 5.4 and 9.5 were negative.



SI Figure 2. Zeta potential of SiO₂ nanoparticles.

The deposition of SiO₂ nanoparticles was greatly influenced by the applied voltage, despite the PAH polymer chain conformation existing in the coiled structure. We also measured the amount of adsorption of each layer and estimate the amount of adsorption of PAH and SiO₂ inside 5 layer film by QCM. The amount of adsorption of PAH and SiO₂ inside the (PAH 3.9/SiO₂ 5.4)₅ film fabricated without and under applied voltage was shown in **SI Figure 3**. The weight ratio between PAH and SiO₂ nanoparticles was 6:94 for film fabricated without applied voltage and 13:87 for the film fabricated under applied voltage of 0.5 V and 8:92 for the film fabricated under applied voltage of 1.0 V. Therefore, the weight ratio between PAH and SiO₂ nanoparticles was almost unchanged by applied voltage.



SI Figure 3. Amount of adsorption of PAH and SiO₂ inside the (PAH 3.9/ SiO₂ 5.4)₅ films fabricated without and under applied voltage of 0.5 V and 1.0 V.