Spin-Assembled Layer-by-Layer Films of Weakly Charged Polyelectrolyte Multilayer

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We investigate the effect of film deposition methods on the film properties of layer-by-layer assembled polyelectrolyte multilayers. Multilayered structures of linear polyethylenimine (LPEI) and poly(acrylic acid) (PAA) are prepared by using conventional dipping-based assembly as well as spin-assisted assembly. While the polyelectrolyte interpenetration by the diffusion motion of LPEI species is allowed in dipping-based assembly, an instantaneously and kinetically frozen phase of the film deposition is obtainable from spin-assisted assembly. Being kept from the interdiffusion of LPEI, a stratified internal structure is expected in the spin-assisted assembly, which is completely contrasted to the intermixed phase in the dipping-based assembly. The ability to control the inner structure of the multilayered film enables us to manipulate the physical properties or chemical activity of the functionalized thin films. We also demonstrate that the control over the strength of polyelectrolyte interdiffusion on a very top surface can be utilized for a quantitative manipulation on the degree of macromolecular self-assembly of nanomaterials.

Keywords: Spin Assembly, Layer-by-Layer Assembly, Thin Film Deposition, Weakly Charged Polyelectrolyte Multilayers, Linear Polyethylenimine, Viruses.

1. INTRODUCTION

Electrostatic layer-by-layer (LbL) self-assembly of polyelectrolyte multilayers has attracted much attention as one of the most versatile and convenient techniques for constructing controlled nanostructures through the manipulation of molecular interactions.[1, 2] The technique is mainly based on the sequential adsorption of polyelectrolytes containing complementary charged groups from aqueous solutions to form ionically complexed thin films. During the LbL self-assembly, polyelectrolytes from solutions form electrostatically bound complexes with polyelectrolyte functional groups of opposite charges that are present on the surface, leaving excess charges upon adsorption due to charge overcompensation. Therefore, the surface charge of the outermost layer is altered between the anionic and cationic state, and this charge reversal offers a driving force for the sequential build-up of multilayers in the LbL assembly. As a result, one can obtain a more or less irreversibly adsorbed polyelectrolyte multilayer of which thickness and interpenetration can be readily manipulated

with varying the type of adsorbing species and processing conditions such as polyelectrolyte charge, ionic strength, salt concentration and adsorption time.[3, 4]

Conventionally used dipping-based LbL self-assembly utilizes three major steps for a film deposition: (1) the diffusion of polyelectrolytes from the solution medium to a substrate, (2) the adsorption of polyelectrolytes on the surface via molecular interactions, (3) the molecular rearrangement of polymeric chains along the surface for the formation of equilibrated phase.[1] Varying the aforementioned processing conditions in each step, one can readily manipulate the deposition process of polyelectrolyte chains and eventually obtain the controllability over the film properties of deposited layers. Although the robustness of the dipping-based process has been confirmed, however, it is generally recognized that this process is excessively time-consuming and a complete process to achieve adsorption equilibrium requires hours even to days. Considering this throughput limitation, a few alternative methods such as spray-assisted LbL assembly and spin-assisted LbL assembly have been suggested toward developing more rapid and straightforward processing.[5–7] In particular, the spin-assisted LbL assembly using a highly applied shear force

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has been extensively investigated due to its advantages in alleviating surface roughness and interpenetration, as compared to the dipping-based LbL assembly.[7–9]

Another notable aspect of the LbL self-assembly is that it usually leads to a linear growth in film thickness as exemplified in the case of many strongly charged polyelectrolyte multilayer systems. Strong charge binding between ion pairs yields an ionically crosslinked network, from which an identical increase in stepwise film thickness can be obtained (linear growth).[10, 11] However, many studies have reported cases of the LbL assemblies in which the films exhibited a super-linear or exponentially growing film thickness with increasing the number of polyelectrolyte deposition layers.[12, 13] Investigations revealed that this phenomenon was specifically observed in weakly charged polyelectrolyte multilayer systems. It can be attributed to the reversible interdiffusion of at least one of the polyelectrolyte species that constitute the film. By using this interdiffusion process of polyelectrolytes, recently, we have shown that supramolecular-sized viruses can be self-assembled and highly ordered on the surface of a weakly charged polyelectrolyte multilayer, which is potentially beneficial for a construction of highly integrated nanostructures.[14–17]

In the present study, we explored the process of spin-assisted LbL assembly for a weakly charged polyelectrolyte pair of linear polyethylenimine and poly(acrylic acid) and compared the film properties to those obtained from dipping-based LbL assembly. As opposed to the exponential film growth in the dipping-based method due to the enhanced interdiffusing mobility of weakly charged polyelectrolytes, here, the kinetically frozen and mobility-limited deposition of polymer chains during spin-coating leads to a linear but retarded growth in film thickness. In spite of the limited surface mobility of polyelectrolytes in this case, however, an ordered phase of viruses can be achieved under certain pH ranges of the coating solution, indicating that it is required a minimum thickness of polyelectrolyte for inducing a macromolecular self-assembly on the surface.

2. EXPERIMENTAL DETAILS

2.1. Materials Preparation

Cationic LPEI ($MW = 25$ kDa, Polysciences) and anionic PAA ($MW = 90$ kDa, 25% aqueous solution, Polysciences) were used as received and diluted in deionized water to prepare 35 mM and 20 mM solutions on a repeat unit basis, respectively. Due to its linear and regular structure, LPEI forms a crystalline solid when unprotonated and is thus insoluble in water above its pKa. To dissolve LPEI into water, a small amount of HCl solution was added to a mixture of LPEI and deionized water until all the LPEI was dissolved. The pH of both solutions was carefully adjusted to a range from 3.5 to 6.0 with diluted solutions

of HCl and NaOH. Silicon substrates were first plasma-treated with a conventional plasma cleaner for 30 sec (PDC-001, Harrick Scientific Corp.) to prepare a negatively charged initial surface.

2.2. Layer-by-Layer Deposition of Polyelectrolyte Multilayer

Spin-assisted LbL films were prepared by using an automatic spin-coater (Midas system, Spin-1200D). Polyelectrolyte solutions of LPEI and PAA were alternatively spun coated (25 sec at 3500 rpm) onto the silicon substrate with two additional washing steps (Milli-Q water) between the layer depositions (Fig. 1(a)). For the LbL assembly by the dipping method, a HMS programmable slide stainer (Zeiss) was used with a deposition condition of 15 min adsorption of polyelectrolyte solutions, followed by three sequential washing steps in the bath of deionized water (Fig. 1(b)). The resulting multilayer is denoted as (Polymer A/Polymer B m/n)$_X$, where X is the number of layer pairs of cationic polymer A and anionic polymer B, and m and n are the solution pH of Polymer A and B, respectively. When $X =$ (the number of bilayers $+$ 0.5), the cationic polymer A is the finally adsorbed layer, thus the outermost surface of the multilayer.

2.3. Self-Assembly of M13 Viruses on Polyelectrolyte Multilayer

Wild type M13 viruses were amplified using bacterial medium (*Escherichia coli* strain ER2738, New England Biolabs) and diluted in water to a final concentration of $10^9 \sim 10^{10}$ molecules/ml. For an ordered assembly of M13 viruses on polymer deposited films, the solution pH of virus was adjusted to 4.8, near the isoelectric point of

(a)

(b)
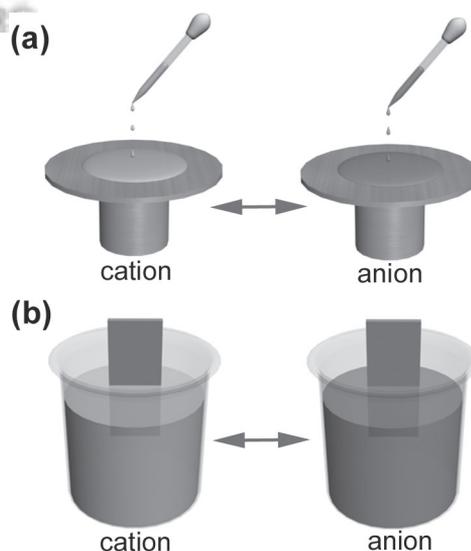
Fig. 1. Schematic illustration of the experimental procedure. (a) Spin-assisted LbL assembly. (b) Dipping-based LbL assembly.

M13 virus. Then, the virus solution was drop-dispensed on the prepared polymer surface for 20∼30 min at ambient temperature. During the adsorption process, negatively charged M13 viruses were electrostatically bound on the positively charged top surface of the LPEI/PAA multilayer. Depending on the interdiffusion ability of LPEI species in the polyelectrolyte multilayer structure, surface adsorbed viruses could be assembled and reorganized to highly ordered structure. Virus assembled surfaces were rinsed with deionized water several times to remove loosely bound viruses and dried by nitrogen blowing.

2.4. Characterization of Films and Surfaces

The thickness of the deposited layer was measured by ellipsometry (Nanoview, SE MF-1000). The surface topology and roughness of spin-assisted LbL films and virus assembled surfaces were characterized with AFM (Veeco, Innova) in dry condition. In order to minimize any possible misreading during data acquisition and to enhance the image resolution, we used slow scanning tapping mode (0.5∼1.0 Hz of a scan speed).

3. RESULTS AND DISCUSSION

Figure 2 shows a difference in film growing characteristic between the spin-assisted LbL and dipping-based LbL process. As shown in Figure 2(a), a previous investigation on the LPEI/PAA film prepared from a dipping method reveals that the exponential growth is prominent when the film is deposited under a pH condition between 4.0 and 5.0.[16] At this condition, cationic LPEI chains are partially charged (pKa of LPEI ∼ 5.5) and a portion of LPEI chains are free to move around the inner structure of ionic complexes of LPEI and PAA. Due to its unique characteristic of LPEI interdiffusion, an excess amount of LPEI can be stored in the film, which yields a super-linear (exponential) growing characteristic in the film growth. As seen in Figure 2(b), however, the spin-assisted LbL assembly generates linearly growing films, irrespective of the pH condition of coating solutions. It can possibly be ascribed to the highly applied centrifugal and shear forces during spin-coating, such that the amount of polyelectrolyte chains adsorbed on the surface is strongly regulated by the spin-coating process.[7] The fastest growing condition was observed around at pH 4.8 deposition condition, at which pKa values of both polyelectrolytes are contiguous.

It should be noted in this regard that the film growth in the spin-assisted LbL of LPEI/PAA is much slower than that in the dipping method. It is contrary to the previously reported case of the spin-assisted LbL system such as PAH/PSS (poly(allylamine hydrochloride) and poly(sodium 4-styrenesufonate)), in which the electrostatic binding between polymer chains plays a dominant role on the LbL assembly and the film grows much faster
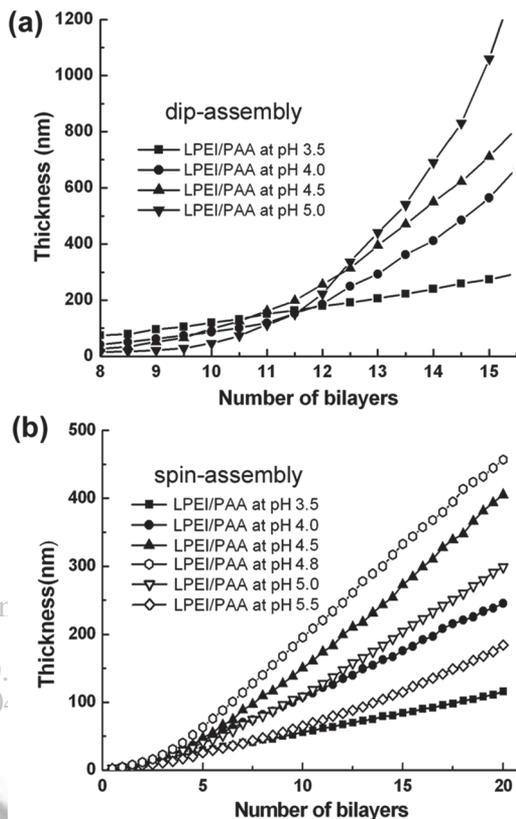
Fig. 2. Comparison of thickness growth curves between dipping-based and spin-assisted assembly of LPEI and PAA measured using ellipsometry. (a) Super-linear growth in dipping-based LbL assembly. (b) Linear growth in spin-assisted LbL assembly.

than in the dipping-based deposition. It is originated from 'concentration thickening effect' due to a fast removal of solvent during a spin-coating process. In the LPEI/PAA LbL system, however, the interdiffusion of free chains of LPEI rather than a simple electrostatic binding governs the mechanism of the sequential deposition of layers. Therefore, a very short period of LPEI adsorption in the spin-assisted LbL assembly can effectively block the interpenetration and interdiffusion of LPEI chains, leading to a retarded growing characteristic as compared to the dipping-based assembly of LPEI/PAA. Similar tendency of reversal in a film growing speed between the spin-assisted and dipping-based LbL assembly has been also reported in the hydrogen-bonding LbL system.[18]
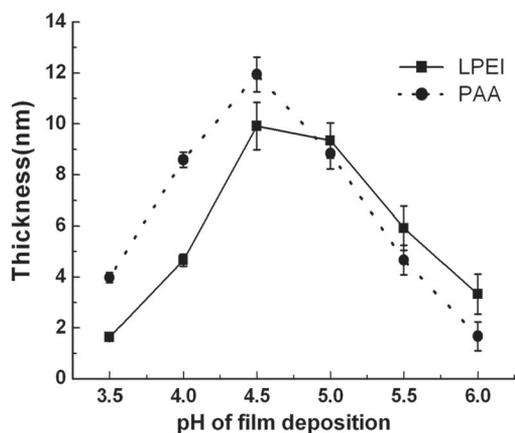
The surface roughness of LbL films was also investigated to compare the influences of different deposition methods. As shown in Figure 3(a), the RMS (root-mean-square) roughness of spin-assisted films measured from AFM remains consistently at around 1 nm, which is nearly flat as verified from Figure 3(b). Clearly separated interfaces between layers confirm that the interpenetration and interdiffusion of LPEI species is strongly suppressed inside the films. In contrast, it was found that the RMS roughness of dipping-based films is generally larger than that of spin-assembled films and the value fluctuates depending
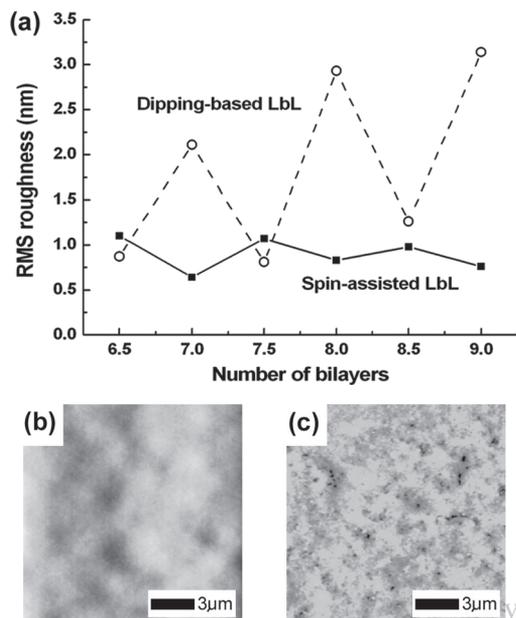
Fig. 3. Comparison of RMS surface roughness between dipping-based and spin-assisted assembly of LPEI and PAA characterized using atomic force microscopy (AFM). (a) Surface roughness maintains almost constant for spin-assisted assembly while it fluctuates for dipping-based assembly. (b) AFM image for a surface of (LPEI/PAA 4.5/4.5)$_{9.0}$ prepared from spin-assisted LbL assembly. (c) AFM image for a surface of (LPEI/PAA 4.5/4.5)$_{9.0}$ prepared from dipping-based LbL assembly (scan size = 15 μm × 15 μm, Z-range = 20 nm).

Fig. 4. Averaged stepwise increment in film thickness with respect to a variation in pH condition of polyelectrolyte solutions in spin-assisted LbL assembly. Fastest film growing is observed within pH range of 4.5~5.0.

on the type of polyelectrolytes atop the surface. During the LPEI deposition in the dipping-based assembly, LPEI chains in the solution make 'diffusion-in' motion into the inner structure of the film and the surface accordingly shows a very flat condition. When the sample is placed under complementary charge deposition (PAA), however, LPEI chains stored in the film make 'diffusion-out' motion toward the solution medium for maximizing electrostatic bindings with PAA chains, which leaves a roughened structure on the surface (Fig. 3(c)).[14]

In order to rationally characterize the film properties of spin-assisted LbL films, it is necessarily required to know the relative composition of LPEI and PAA in the LbL assembled films. As the interface between LPEI and PAA is flat and smooth as confirmed from the roughness analysis, we can assume that the relative composition is simply proportional to the stepwise increment in film thickness. The results are summarized in Figure 4. The stepwise increase in the film growth shows a Gaussian distribution for both LPEI and PAA and reaches the maximum within pH 4.5~5.0 deposition condition, which matches well with the overall thickness-growing characteristics presented in Figure 2. When the film deposition is performed under relatively lower pH conditions (pH < 4.5), cationic LPEI is highly charged and anionic PAA is less charged, leading to a PAA rich composition. On the other hand, in the deposition process carried out

under relatively higher pH conditions (pH > 4.5), the ionization of LPEI is weakened and that of PAA is proliferated, therefore, an inversion in the film composition takes place.

The relative composition of LbL films created using different deposition methods was compared in Figure 5. It should be addressed that the dipping-based LbL assembly at higher pH conditions is unable to achieve because of the enhanced desorption of LPEI chains from the film surface. As shown in Figure 5, the composition variation is more prominent for the spin-assisted LbL assembly. A variation in the degree of ionization of polyelectrolytes depending on the pH condition accordingly gives rise to a wide range of variation in the relative composition of the assembled films (LPEI composition varies within 30~70%). In the course of the spin-assisted LbL assembly, the charge density of polyelectrolyte chains is directly critical to the
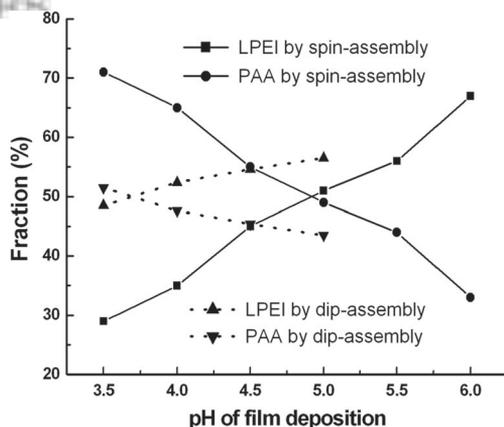
Fig. 5. Analysis of fractional compositions of LPEI and PAA in LPEI/PAA films; solid lines for spin-assisted LbL assembly and dotted lines for dipping-based LbL assembly. Generally, as the film deposition pH is increased, the degree of ionization of LPEI decreases and vice versa for PAA. As a result, the relative composition of LPEI in the complexed film also increases.

chain conformation in electrostatic binding between oppositely charged polyelectrolytes: a stretched chain conformation under a highly ionized condition and a coiled (entangled) conformation under a slightly charged condition, from which the overall structure of ionic complexes can be determined. On the other hand, for a dipping-based LbL assembly of LPEI and PAA, the interdiffusion of LPEI is freely allowed and the pre-deposited LbL film thus can be used as a reservoir of free LPEI chains. Accordingly, the relative composition of LPEI is less sensitive to the change in the pH condition of film deposition (relative composition of LPEI varies within 40~55%).

It has been investigated that the considerably vigorous interdiffusion of LPEI in LbL deposited films can be utilized for inducing a self-assembly of macromolecular species such as viruses (Fig. 6(a)).[14–17] Conversely inspired by this unique characteristic of LPEI, viruses could be used as tracers to estimate the surface mobility of LPEI quantitatively. This idea can be adopted to this study of spin-assisted LbL assembled films. Because the interpenetration or interdiffusion of LPEI is strongly suppressed in this system, a limited amount of LPEI chains placed in the outermost layer can only take part in inducing the self-assembly of viruses. Based on this understanding, we can expect to estimate the minimum thickness of LPEI layer

that is required for a viral self-assembly, which will be potentially useful for designing a polyelectrolyte platform to drive the self-assembly or self-organization of a variety of nanomaterials.

Notably, as similar to the viral ordering onto the dipping-assembled film, a well-ordered phase of viruses was obtained atop the surface of the spin-assisted LbL film prepared at pH 4.8 condition (Fig. 6(b)). It seems that a LEPI layer with an approximately 10 nm thickness covers the outermost surface, as can be inferred from data of the stepwise increase in thickness presented in Figure 4. Considering the fact that the diameter of the M13 virus is 8.8 nm, which is slightly smaller than the LPEI layer thickness, the result of complete viral ordering is reasonably acceptable. However, when the viruses were placed onto the LbL assembled films prepared at pH 4.0 or pH 5.5, only a small amount of viruses were bound to the LPEI coated surface in a less ordered way. It can be attributed to the fact that the underlying LPEI layer (~5 nm) is much thinner than the diameter of the viruses, on which the surface mobility of LPEI is not adequate for deriving the macromolecular motion of surface adsorbed viruses.

4. CONCLUSIONS

In this study, we have compared the spin-assisted layer-by-layer assembly of a weakly charged polyelectrolyte multilayer of LPEI and PAA to the dipping-based assembly. The quasi-quenched deposition of polyelectrolytes in the spin-assisted assembly where a fast rate of solvent removal and subsequently accompanied shear force are strongly applied can effectively block the interpenetration and interdiffusion of LPEI, leading to the formation of a slowly and linearly growing LbL films. In contrast, the interdiffusion of LPEI is vigorously activated in the dipping-based assembly. Investigations on the surface roughness and the relative composition of constituting polyelectrolytes strongly support this explanation. Additionally, the minimum thickness of LPEI for inducing a macromolecular self-assembly is indirectly estimated via attaching the one-dimensionally shaped anisotropic viruses onto the surface of the spin-assembled LPEI. The spin-assisted LbL assembly is a robust and straightforward technique that can allow one to alter the inner structure of multilayered films in a simple and time-efficient way. If further tailored and controlled, it is anticipated that an economically viable and facile processing technique for the fabrication of function-integrated thin film devices can be presented.[19, 20]
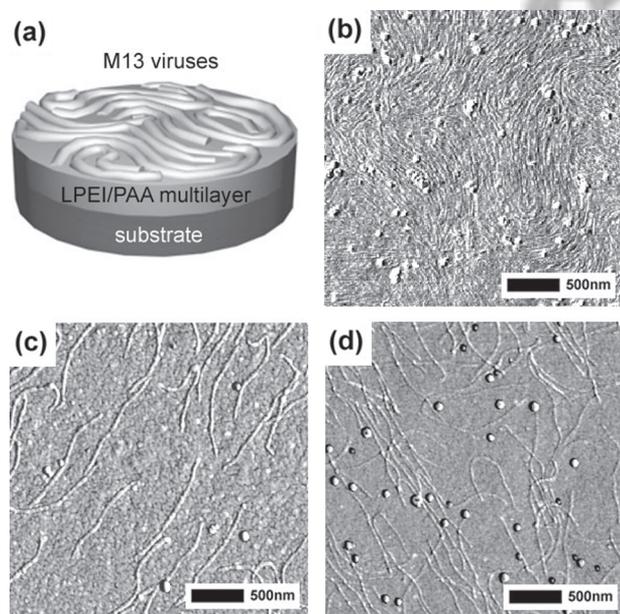
Fig. 6. Virus assembly on spin-assisted LbL films of LPEI and PAA. (a) Schematic illustration for virus assembly. Negatively charged M13 viruses are electrostatically bound onto the positively charged LPEI surface and subsequently reordered to non-overlapped structure driven by the surface mobility of free LPEI chains. (b) Phase mode AFM image of a successful virus ordering on film of (LPEI/PAA 4.8/4.8)$_{10.5}$. (c, d) Phase mode AFM images of little virus binding and ordering on films of (LPEI/PAA 4.0/4.0)$_{15.5}$ and (LPEI/PAA 5.5/5.5)$_{15.5}$, respectively. AFM images were captured under dry condition with a scan area of 3 μm × 3 μm and Z-range is 20 degrees.

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