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Electric-Field-Assisted Layer-by-Layer Assembly of Weakly Charged Polyelectrolyte Multilayers

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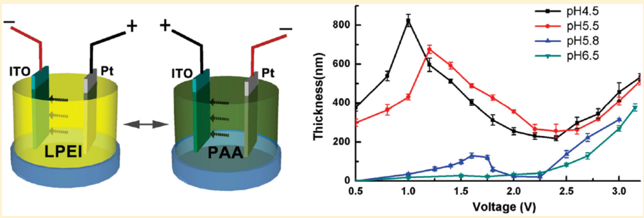
ABSTRACT: We describe how layer-by-layer (LbL) assembly of weakly charged polyelectrolytes can be controlled by applying an electric field (electrophoretic LbL deposition). The rate of deposition of polyelectrolytes of cationic polyethylenimine (LPEI) and poly(acrylic acid) (PAA) can be enhanced by increasing the magnitude of the externally applied electric field. Accordingly, a micrometer-thick film can be attained by electric-field-assisted LbL assembly with the deposition of less than 10 bilayers. However, the ionization conditions or electrostatic mobility of weakly charged polyelectrolytes is highly influenced by the environmental conditions of the polyelectrolyte solution, resulting in complex film deposition behaviors in response to the variation of the electric field strengths. At an intermediate electric field strength, the adsorption of polyelectrolytes is weakened due to the electrolysis of water at the electrode surface and a subsequent reduction in the degree of ionization of the polyelectrolyte chains. However, under a strong electric field, reinforced electrophoretic deposition of polyelectrolyte chains overwhelms the effects of the electrolysis of water, leading to enhanced LbL film assembly. By exploiting this phenomenon, we were able to achieve successful film deposition even at pH values that are typically not available in the conventional LbL assembly. Additionally, we demonstrated that our method could be used to pattern the polyelectrolytes via selective deposition onto suitable electroconductive substrates for various downstream applications.



INTRODUCTION

Layer-by-layer (LbL) assembly of charged polyelectrolytes has been investigated extensively in the past two decades across a broad set of applications ranging from functional coating,[1,2] optical surfaces,[3] next-generation electronic devices,[4] smart drug delivery systems,[5] to high capacity energy devices.[6] Conventional LbL assembly of polyelectrolytes primarily takes advantage of the electrostatic interactions between complementarily charged species of polyelectrolytes as the driving force for multilayered deposition. Because this method exploits the inherent charged properties of materials under dipping-based aqueous conditions, the entire process of LbL assembly is very simple and can be easily scaled up.[1,7,8] Moreover, it allows for the charged binding of polyelectrolytes to other materials, such as inorganic nanoparticles, carbon nanotubes, or biomolecules, thereby providing a versatile platform for hybridizing multiple functionalities into the assembled films.[9−11]

Although controlled deposition of film with regard to targeted composition, thickness, and stacking order is possible using LbL assembly, the use of polyelectrolyte multilayers, which relies on sequential adsorption in a solution phase, is occasionally limited by the long processing time required relative to spin-coating or film casting-based deposition methods.[12,13] To achieve film buildup during LbL assembly, excess charge that exists on the surface is alternately switched by sequential adsorption of oppositely charged polyelectrolytes, thereby inducing electrostatic attraction and subsequent ionic complexation. Therefore, when polyelectrolyte chains are highly charged and stretched, the deposited film grows linearly in proportion to the number of polyelectrolyte adsorptions.[7,14] However, recent studies have revealed that LbL-assembled films are able to grow exponentially when the polyelectrolytes are able to interdiffuse within the complexed film.[15−19] These systems enable high-speed film buildup with a relatively small number of polyelectrolyte adsorption and facilitate industrial-scale application of LbL assembly.

Though the characteristics of LbL multilayer deposition can vary according to the intrinsic physical properties of the polyelectrolytes, such as the type of the polymeric main chain, the molecular weight, or the attached functional group, they can also be manipulated by external factors,[20] such as the ionic strength of the dissolved salts or the pH of the polyelectrolyte solution.[21,22] In particular, for weakly charged polyelectrolytes whose surface charge can vary according to the environmental pH value, the success of film deposition by LbL assembly is determined by the correlation between the pK_a values of the polyelectrolytes and the pH of the solution. By manipulating the pH, the degree of ionization of the polyelectrolytes can be adjusted for electrostatic assembly.[23−25] To obtain successful film deposition,

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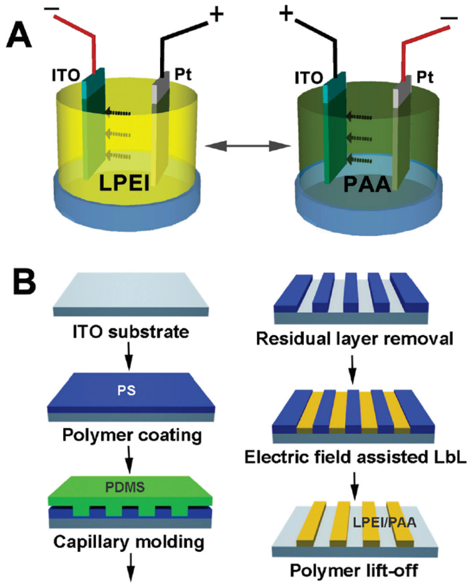

Figure 1. Schematic illustrations of electric-field-assisted LbL assembly and pattern formation. (A) For electric-field-assisted LbL assembly of LPEI and PAA, a negative bias was applied for LPEI adsorption and a positive bias for PAA adsorption, alternately. (B) Capillary molding was employed to create negatively replicated line patterns of polystyrene, followed by electric-field-assisted LbL deposition onto the polymeric template for selective deposition of polyelectrolytes, resulting in the deposition of positively patterned structures of LPEI/PAA ionic complexes.

the pH values used in LbL assembly should fall within a specific range. In recent studies, an external electric field was employed during LbL assembly to trigger the charge characteristics of the polyelectrolytes.[26−30] Application of an electric potential to the substrate enabled an enriched polymeric adsorption and enhanced rate of film deposition. However, few polyelectrolyte pairs have been tested, and the charge characteristics of polyelectrolytes and subsequent film deposition under an electric field have not been examined systematically.

We investigated electric-field-assisted LbL assembly (electrophoretic LbL deposition) of weakly charged polyelectrolytes under a wide range of electric fields, and we report on film growth in response to the applied electric field. The rate of film deposition of the polyelectrolyte pair of LPEI and PAA was enhanced under an electric field due to charge-enhanced surface adsorption. Unexpectedly, however, we also found that the growth of the film varied in a nonmonotonic manner according to the strength of the applied electric field. This phenomenon can be attributed to competition between the surface adsorption of polyelectrolyte chains and the electrolysis of water under an applied electric field; the latter affects the local pH of the polyelectrolyte solution near the electrodes. Thus, film may form even at pH values that are prohibitive for conventional LbL assembly. Furthermore, selective film deposition onto conductive patterns can enable spatially controlled deposition of polyelectrolyte multilayers. We anticipate that our proposed approach can be applied to produce pH-sensitive surface coatings or design functionalized hybrid materials for biological applications.

EXPERIMENTAL SECTION

Preparation of Polyelectrolyte Solutions. Linear polyethylenimine (LPEI, 250 000 M_w, monodispersed, Polysciences) and poly(acrylic acid) (PAA, 90 000 *Mw*, polydispersity index (PDI) ~ 4, 25% aqueous solution, Polysciences) were used as-received and prepared as 35 and 20 mM solutions in deionized (DI) water, respectively, based on the repeat-unit molecular weight. Because of its linear and regular structure, LPEI forms a crystalline solid when unprotonated and is thus insoluble in water above its pK_a. To dissolve LPEI into water, therefore, a small amount of hydrochloric acid solution was added to a mixture of LPEI and deionized water until all the LPEI was dissolved.[31] The pH of both solutions was adjusted to a range between 4.0 and 10.0 carefully with diluted solutions of hydrochloric acid and sodium hydroxide.

Electric-Field-Assisted LbL Assembly. Indium tin oxide glasses (ITO, Samsung Corning Precision Materials, Korea) as the substrate (working electrode) and a platinum mesh as the counter electrode were cleaned by sonication in acetone, methanol, and DI water for 5 min, respectively. Polyelectrolyte multilayers were assembled on prepared ITO glass substrates by using a programmable slide stainer (HMS70, Microm, Germany) with a deposition condition of 5 min adsorption of polyelectrolyte, followed by three sequential washing steps in a DI water bath. The nomenclature $(\mathrm{LPEI/PAA})_X$ will be used to denote a multilayer film of X layered pairs of LPEI and PAA. When X includes 0.5, LPEI is the final adsorbed layer and thus the outermost surface of the multilayers. For electric-field-assisted LbL assembly of polyelectrolytes as shown in Figure 1A, a direct current (dc) power supply (dc power 303DS, Digital Electronics Co., Korea) was connected between the ITO glass substrate and the Pt counter electrode, with a consistent distance of 3 cm. An applied voltage was varied from 0.5 to 4.0 V (±0.01 V), measured between the electrodes. To enhance the adsorption of the polyelectrolytes onto the ITO substrate, a negative bias was applied to the ITO substrate during the cationic LPEI adsorption and a positive bias was applied to the anionic PAA adsorption, alternately. The electric field was applied until the washing steps, and then it was switched to the opposite charge for the next step of polyelectrolyte adsorption. All experiments of LbL assembly were performed under ambient conditions.

Pattern Formation by Electric-Field-Assisted LbL Assembly. The experimental procedure used for patterning is schematically depicted in Figure 1B. For the selective deposition of polyelectrolytes onto a conducting substrate of ITO, patterns of polystyrene (PS) were prepared on the ITO substrate as an electric field blocking layer. A capillary molding process was adopted for the patterning of the PS.[32] First, the ITO substrates were spin-coated with PS (350 000 M_w, Aldrich) in toluene to the desired thickness, approximately 200−300 nm. The samples were, in turn, baked in a vacuum oven at 70 °C for 1 h in order to remove any residual solvent in the polymer film. Next, a polydimethylsiloxane (PDMS) mold that was a negative to the silicon master pattern was placed on the polymeric film, and a uniform contact was ensured. Subsequently, the temperature of the samples was elevated to 120 °C above the glass transition temperature of the polymer (T_g of PS ~ 100 °C), while applying a slight pressure of 0.5 to 1.0 MPa for 2 h. After the molding process, the PDMS mold was carefully removed; the thin residual layers of PS remaining at places where the PDMS mold had been in contact were removed by a short plasma treatment (air plasma, 1 min) using a conventional plasma cleaner (PDC-001, Harrick Scientific Corp.).[33] Next, the electric-field-assisted LbL process was applied for a selective adsorption of LPEI and PAA polyelectrolytes onto templated regions surrounded by PS patterns. Finally, since ionically complexed LPEI/PAA patterns were not subject to the swelling in organic solvent environments, PS patterns were removed by a lift-off processing in toluene, leaving a patterned structure of an LPEI/PAA ionic complex on the ITO substrate.

Characterization of LbL-Assembled Film. The changes in film thickness of the assembled polyelectrolyte multilayers in response to the assembling pH value and the strength of applied electric field were measured by ellipsometer (SE MF-1000, Nanoview, Korea), alpha-step surface profiler (HRP350, KLA Tencor), and atomic force microscope (AFM, Dimension 3100, Veeco) under dry condition. The current−voltage characteristics of

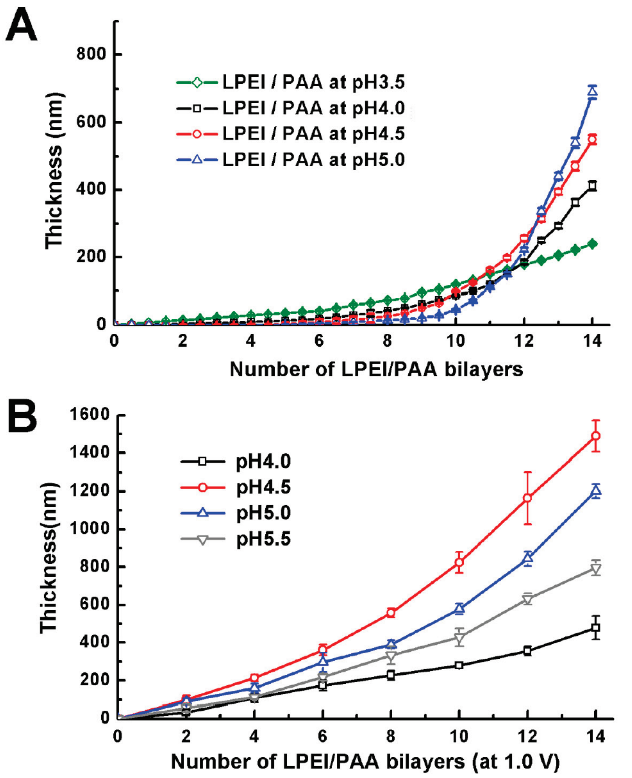

Figure 2. Ellipsometric observations of film thickness growth of LPEI/PAA multilayers at different pH conditions with or without an applied electric field. Error bars indicate standard deviations. (A) Conventional assembly without an applied electric field. (B) Electric-field-assisted LbL assembly at an electric potential of 1.0 V. The fastest film deposition was observed at a pH of 4.5.

the LbL-deposited ITO glass was investigated with semiconductor parameter analyzer (CHI608C, CH Instruments) with Ag/AgCl reference electrode. To visualize the patterned structures of electric-field-assisted LbL assembled films, samples were observed with scanning electron microscope (SEM, JSM-7401F, JEOL, Japan).

RESULTS AND DISCUSSION

To assemble the weakly charged polyelectrolytes of LPEI and PAA using electric-field-assisted LbL assembly, we applied a dc electric field between the ITO substrate and Pt counter electrode with a fixed interspacing distance of 3 cm. While plasma treatment is usually used for LbL assembly on a silicon or glass substrate to obtain adequate hydrophilicity and surface charges for the initial adsorption of polyelectrolyte chains,[19] we did not employ a pretreatment procedure for the ITO glass substrate because ITO surfaces are intrinsically strongly negatively charged.[26] An open-circuit voltage that could facilitate a minimum effect of the electric-field-assisted LbL was observed at 0.5 V. Below this electric potential, LbL-assembled films have similar growth characteristics to conventional nonelectric field assisted LbL-assembled films. Therefore, in this study, we used an electric field strength greater than 0.5 V for the electric-field-assisted LbL assembly of LPEI and PAA polyelectrolytes.

The results of film deposition of LPEI/PAA multilayers in the absence of an electric field are shown in Figure 2A; successful ionic complexation of LPEI and PAA occurred in the pH range between 3.5 and 5.0. Because the pK_a values of LPEI and PAA are known to be located around 5.5 and 6.5, respectively,[23−25,34,35] this polyelectrolyte pair can easily be assembled due to electrostatic interactions at this given pH range at which the polymeric chains maintain a moderate degree of ionization. Because of the remarkable interdiffusing ability of LPEI, film growth showed two contrasting behaviors according to the fractional content of LPEI within the film and its degree of ionization: linear growth at a relatively low pH (~pH 3.5) and exponential growth at a relatively high pH (~pH 5.0).[19] When film growth was exponential, film less than 100 nm thick was obtained at the early stage of film deposition; after around 10 bilayer adsorptions, however, film deposition accelerated remarkably and a 1 μm thick LPEI/PAA complexed film was obtained after 15−16 bilayer depositions.

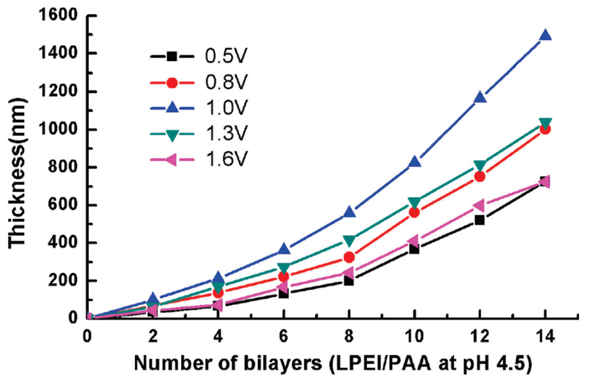

Figure 3. Ellipsometric observations of the growth of LPEI/PAA multilayers at different electric field strengths. The fastest film deposition occurred at an electric field strength of around 1.0 V.

Electric-field-assisted LbL assembly can amplify this growing characteristic more significantly. As shown in Figure 2B, when an electric field of 1.0 V was applied, LbL deposition of 10 bilayers at a pH of 4.5 yielded a 800 nm thick LPEI/PAA film. Although exponential growth still occurred when an electric field was applied, but it showed a mitigated tendency compared to the nonelectric field applied condition, indicating that the accelerated film growth was dominantly attributed to the externally applied electric field rather than an intrinsic nature of the interdiffusion of LPEI. By applying a negative bias to the ITO substrate, the adsorption of LPEI was accelerated, and by applying a positive bias to the substrate, the adsorption of PAA was also enhanced, facilitating greater ionic complexation between LPEI and PAA. It should be noted that the film deposited by electric-field-assisted LbL assembly (electrophoretic LbL deposition) retained its physical and mechanical stability under ambient conditions and various pH conditions, even in the absence of the electric field. Together, these results suggest that electric-field-assisted LbL assembly is a powerful method to increase the speed of film deposition without sacrificing the advantages of conventional LbL assembly methods.

To further characterize electric-field-assisted LbL assembly, we monitored film growth behavior in response to different strength electric fields. Figure 3 shows the results obtained at a fixed pH of 4.5, at which pH film deposition is expected to be the fastest (see Figure 2). The strength of the electric field was modulated in the range of 0.5−1.6 V. We expected that there would be a linear relationship between the magnitude of the applied electric field and the amount of polymer adsorbed on the substrate.[26] In contrast to our expectations, however, we found that there was an optimal electric field strength for the most efficient polyelectrolyte multilayers deposition, as shown in Figure 3. As the electric field was

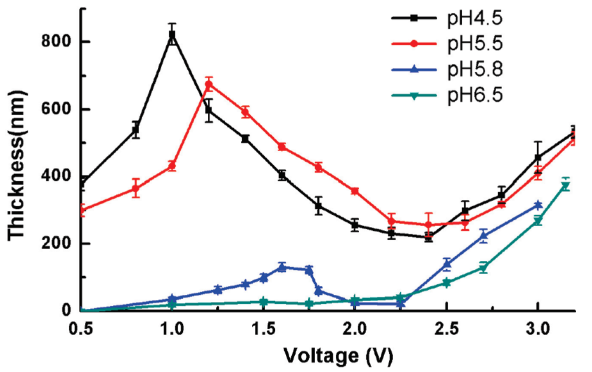

Figure 4. Ellipsometric observations of changes in film thickness of a 10.0 bilayered LPEI/PAA films according to different electric fields strengths and pH conditions. A nonmonotonic change in film thickness was observed. Error bars indicate standard deviations.

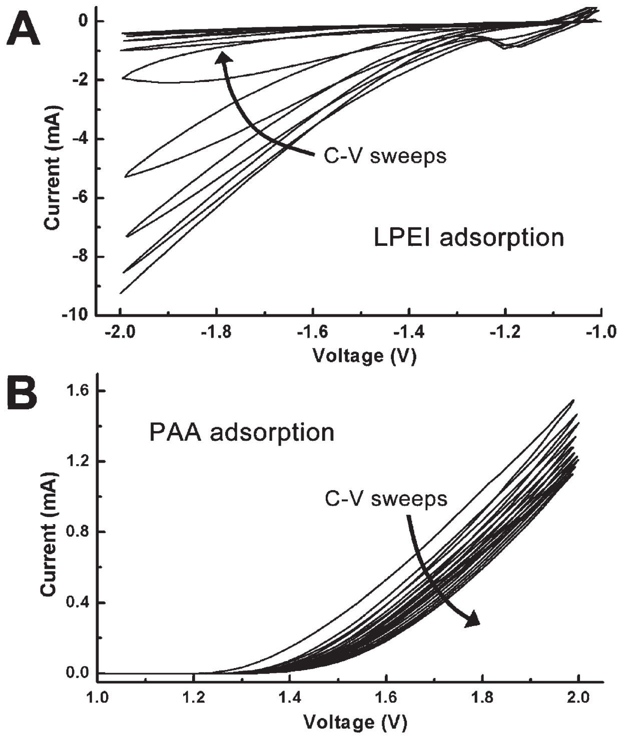

Figure 5. Cyclic voltammetry (CV) characteristic of polyelectrolytes adsorption on an ITO substrate. For measurements, a scan rate of 20 mV/s and an Ag/AgCl reference electrode were used. The current between the electrodes was observed to start flowing at ~1.3 V, which matches the decomposition potential of water. (A) CV characteristics of LPEI adsorption. (B) CV characteristics of PAA adsorption.

increased from 0.5 V (open-circuit voltage) to 1.0 V, a stepwise increment in film thickness during a sequential film deposition also increases, resulting in the thickest deposition of LPEI/PAA multilayers. However, at a field strength higher than 1.0 V, we found that stepwise polyelectrolyte adsorption gradually decreased. Eventually, applying a voltage of 1.6 V yielded nearly identical results to the open-circuit voltage condition of 0.5 V; this implies the existence of competing interactions at higher field strengths that suppress the electrophoretic deposition of polyelectrolyte chains on the surface.

To further explore this phenomenon, we fixed the number of LPEI/PAA bilayer depositions at 10.0 and concurrently varied the assembly pH and the strength of the electric field; the correlation between these variables is summarized in Figure 4. Although the thickness of the deposited film varied according to pH conditions in a rather complex manner, there is a common aspect in the film growth tendency of showing a nonmonotonic behavior, with the coexistence of an intermediate maximum and minimum film thickness. Film thickness reached a first maximum during the early stage of an electric field increase from 1.0 to 1.5 V. Above 1.5 V, the adsorption of polyelectrolytes was mitigated and the thickness of the deposited film gradually decreased, leading to a minimum film thickness at electric field strengths between 2.0 and 2.5 V. However, when the field strength was greater than 2.5 V, the polyelectrolytes adsorbed more strongly again, rendering the nonmonotonic film growth behavior involving the intermediate maximum and minimum. This phenomenon was pronounced for a deposition pH ranging from 4.5 to 5.5 but weakened as the deposition pH increased. At a pH of 6.5, the degree of ionization of LPEI is quite low;[24,36] therefore, at this pH, ionic complexation with PAA rarely occurs, and there is little film deposition, even under an applied electric field of 2.0 V. The various film behaviors shown in Figure 4 suggest that as the strength of the externally applied electric field is varied, the polyelectrolyte chains undergo intricate variations in their chain conformations and degree of ionization.

We attribute this complex interplay between the film deposition pH and the applied electric field primarily to the electrolysis of water and the subsequent suppression of polyelectrolyte adsorption at the electrode surface.[26,28,37] When a weak electric field is applied between the electrodes, the enhanced surface charge of the ITO substrate promotes the attractive adsorption of polyelectrolytes and induces electrophoretic deposition. Because the polarizability of polymeric species, particularly charged polyelectrolytes, is much greater than that of a water molecule,[38] polyelectrolyte chains are expected to show an instantaneous response to the electrostatic attraction under an applied electric field. Therefore, electrophoretic deposition occurs, and the electrostatic compensation process between cationic and anionic polyelectrolytes is reinforced, resulting in the deposition of thicker film of LPEI and PAA.

However, when the strength of the applied electric field is increased to around the decomposition potential of water (1.23 V for pure water, calculated from the Nernst equation), electrolysis of water can occur as follows:[28,39,40]

1. Hydroxide ions are produced at the cathode (e.g., the ITO electrode to which a negative bias is applied during LPEI adsorption)

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \qquad (1)$$

2. Protons are produced at the anode (e.g., the ITO electrode to which a positive bias is applied during PAA adsorption)

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \qquad (2)$$

Because we rarely observed bubble formation (hydrogen or oxygen gas) due to the slow rate of water electrolysis on the electrode surface, we used cyclic voltammetric (CV) measurements to investigate the electrochemical properties of the polyelectrolyte solutions at the electrode surface. As shown in Figure 5, application of either a negative bias to facilitate LPEI adsorption or a positive bias to facilitate PAA adsorption at an applied electric potential of greater than 1.3 V resulted in current−voltage cycles, confirming that the electrolysis of water was occurring.

Water electrolysis and the resulting pH change at localized regions around the electrodes are likely to result in reduced adsorption of LPEI/PAA polyelectrolytes on the ITO substrate and a retarded rate of film growth. For example, during the deposition of LPEI under a negative bias, the degree of ionization of LPEI should decrease in the vicinity of the ITO substrate because hydroxide ions are generated as a result of the cathodic reduction of water, accompanied by an appreciable rise in pH. Similarly, during the deposition of PAA under a positive bias, the degree of ionization of PAA should also decrease near the ITO substrate due to the generation of hydronium ions (anodic oxidation of water), resulting in a drop in pH (more acidic environment). Thus, LPEI and PAA polyelectrolyte chains, which are typical weakly charged polyelectrolytes, are very slightly charged or almost neutral in this environment, eventually leading to a reduced amount of electrostatic binding with counterionic species.

Another thing to be noted in Figure 5 is that the current—voltage cycles with repeated sweeps differed according to the type of polyelectrolyte. During LPEI adsorption, the current at the working electrode gradually decreased as the number of potential sweeps increased. In contrast, during PAA adsorption, the current response to potential sweeps was maintained over repeated cycles. This difference can be attributed to the saturated adsorption of polyelectrolytes during electric-field-assisted LbL assembly. The surface adsorption of LPEI, which has relatively high diffusive mobility compared to PAA, is accelerated by an applied electric field. However, once electrostatic compensation at the surface is complete, saturated adsorption is attained, and the deposited film acts as a diffusion barrier to the underlying electrode. Therefore, no additional water electrolysis occurs, which manifests as a ceasing in the current response with increasing sweep cycles, as shown in Figure 5A. PAA, in contrast, is relatively slowly adsorbed onto the surface; thus, saturated adsorption takes longer than for LPEI. In addition, PAA is prone to be hydrated in an aqueous environment, facilitating continuous electrolysis of water at the surface of the deposited film.

We next investigated why rapid regrowth of film deposition occurred at an applied electric potential of greater than 2.0—2.5 V. A plausible reason for this phenomenon can be a reinforced electrophoretic deposition of polyelectrolytes that overcomes the disadvantageous effects of the electrolysis of water. During LPEI adsorption under a negative bias, the influence of the surface pH change can extend up to around 100 μm from the cathode surface,[41] which is indicative of the thickness of diffusion layer. A basic transition in the diffusion layer near the cathode surface has been well characterized with electrometric methods using micro pH electrodes.[42,43] When an intermediate electric field is applied, the velocity of charged LPEI chains attracted from the bulk solution to the charged ITO substrate is relatively slow.[41,44] Therefore, the degree of ionization of LPEI chains is highly influenced by the increase in pH in the diffusion layer due to the electrolysis of water, which results in a decrease in the amount of LPEI adsorbed to the surface.

When a strong electric field (greater than around 2.0—2.5 V) is applied, the attracting velocity of charged LPEI chains increases in proportion to the applied electric field. In addition, the charged LPEI chains are strongly attracted to the electrode surface within a range of several hundred micrometers to a millimeter apart, which overcomes the reduced adsorption behavior in the relatively thinner diffusion layer wherein the pH rise occurs. Therefore, the attracted LPEI chains can be electrophoretically deposited onto the ITO substrate. During the electrophoretic deposition process, the positively charged LPEI chains react with hydroxide ions that are produced by cathodic reduction of water, yielding unprotonated LPEI chains, which are less soluble in water and can be deposited on the surface. The analogous situation occurs during anodic deposition of PAA under a positive bias; the negatively charged PAA chains react with hydronium ions, leading to the deposition of protonated PAA. As a result, application of an electric field greater than around 2.0—2.5 V eventually results in accelerated LPEI/PAA film deposition.

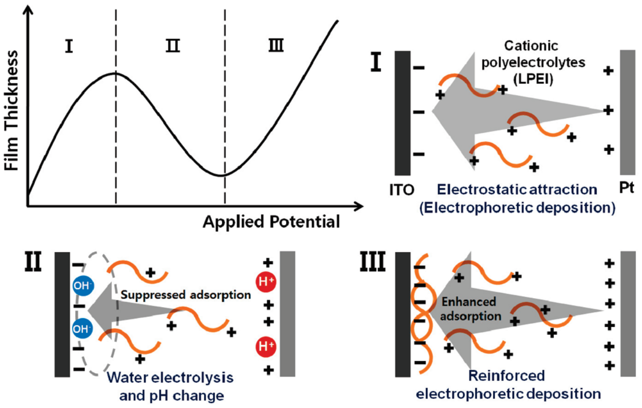

Figure 6. Schematic illustration of nonmonotonic film growth characteristics during electric-field-assisted LbL assembly of weakly charged polyelectrolytes: (I) enhanced polyelectrolyte adsorption under a low electric field, (II) reduced polyelectrolyte adsorption due to the electrolysis of water at an intermediate electric field strength, and (III) reenhanced electrophoretic deposition of polyelectrolyte chains as a result of an increased rate of adsorption at a high electric field strength.

The film growth characteristics shown in Figure 4 are described in Figure 6 as a simplified illustration based on the concepts described above; three regions of film growth can be identified. In region I, charged polyelectrolytes with larger polarizability are strongly attracted by the charged electrode, leading to increased growth under an applied electric field. In region II, an increase in the electric field strength to above the decomposition potential of water results in the electrolysis of water and therefore a substantial pH alteration in the polyelectrolyte solution and a concomitant change in the degree of ionization of the polyelectrolytes, reducing the rate of polyelectrolyte adsorption. In region III, further increasing the electric field strength reincreases the rate of attraction of polyelectrolytes to the charged electrode surface, eventually leading to reinforced electrophoretic deposition of polyelectrolyte chains at the expense of hydroxide/hydronium ions being produced by the electrolysis of water.

The results shown in Figures 4 and 5 suggest that LbL film deposition may be feasible under pH conditions at which the conventional dipping method cannot be used. As discussed earlier, this can be attributed to enhanced electrophoretic deposition of the polyelectrolyte chains under a high-strength applied electric field. For example, LPEI/PAA multilayers cannot be deposited in the pH range from 6.0 and 10.0 using a conventional dipping method because the cationic LPEI (pK_a of LPEI ~ pH 5.5) is less charged under these pH conditions and the electrostatic assembly with PAA is rarely attainable.[24,36] However, by utilizing electric-field-assisted LbL assembly, weakly charged LPEI is readily attracted to the substrate even at a high pH, facilitating electrostatic LbL assembly with anionic PAA. Figure 7 shows the electric potential required to obtain ~200 nm thick LPEI/PAA multilayer films consisting of

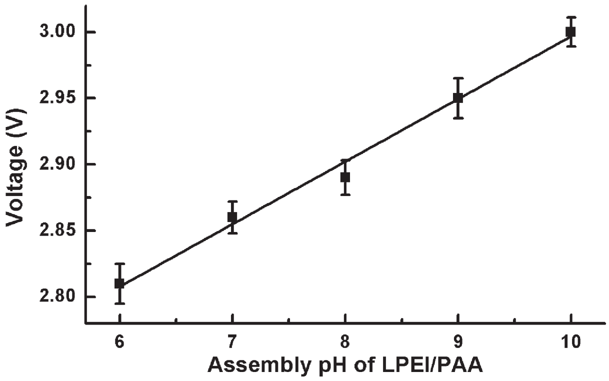

Figure 7. Correlation between the required electric potential and pH during the deposition of 6.0 bilayers of LPEI and PAA to obtain a 200 nm thick film. Error bars indicate standard deviations.

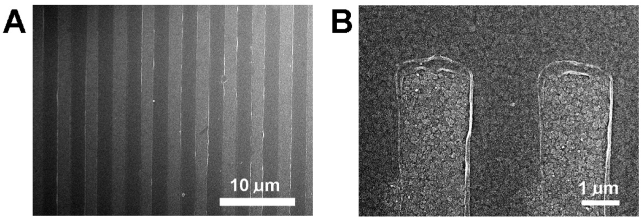

Figure 8. Scanning electron microscopic images of patterned (LPEI/PAA)$_{5.0}$ polyelectrolyte multilayers prepared by electric-field-assisted LbL assembly onto a patterned ITO substrate.

6.0 bilayers. It is clear that LbL assembly of LPEI/PAA at a high pH is possible at an electric field strength of greater than 2.8 V. At higher pHs, the electric potential required for LbL assembly increases accordingly because the LPEI chains should have sufficient attracting velocity to the electrode surface for an electrophoretic deposition to occur. Therefore, we confirm that a successful multilayered film deposition is feasible with the electric-field-assisted LbL assembly even under nonviable pH conditions for the conventional dipping method. In addition, it should be noted that ionically complexed film assembled with the aid of an electric field maintains its mechanical integrity and stability after removal of the applied electric field. However, an excessive increase in an electric field strength of 4.0 V or greater can cause irreversible decomposition damage to the ITO electrode, which can be easily identified as a change in the color of the electrode to a darker color.[45]

To demonstrate the advantages of electric-field-assisted LbL assembly, we performed selective patterning of polyelectrolyte multilayers. If a patterned electrode is employed for electric-field-assisted LbL assembly under pH conditions that are not available for a conventional LbL assembly, polyelectrolyte chains can be selectively deposited on electroconducting patterns of the substrate. This is a result of the selectively occurred electrophoretic deposition of the polyelectrolyte chains only on the patterned regions, while suppressing the nonspecific physical adsorption of polyelectrolytes onto nonpatterned areas. We used capillary molding to prepare patterned structures on the ITO substrate,[32,46] providing a role of the charge screening layer against the applied electric field. Following the procedure introduced in Figure 1B, we prepared a template for the patterned ITO substrate; targeted electroconducting regions were selectively exposed for electric-field-assisted LbL assembly. Next, we performed templated LbL assembly of LPEI/PAA multilayers, yielding a patterned structure of ionic complexes after the lift-off of the polymeric mask layer.

Figure 8 shows a patterned LPEI/PAA multilayer with a line-and-space striped pattern at a spacing of 1.6 μm. For selective patterning of the LPEI/PAA ionic complex, we used a buffered pH value of 7.4 (PBS buffer, 1.0 M) and an applied electric field strength of 3.0 V. The buffered condition was employed to confirm the feasibility of this method under various ionic environments. As a result, a successful demonstration of the patterned LbL assembly was obtained. This patterning strategy can be used to pattern biomolecules or construct biosensing platforms, both of which are highly sensitive to pH conditions during processing.[47]

CONCLUSIONS

The controllability over the characteristics of LbL assembly of weakly charged polyelectrolytes by applying an external electric field was studied. In contrast to previous studies that investigated the continuous adsorption of polyelectrolytes or topological changes of the surface, we exploited the interdiffusing, weakly charged polyelectrolytes of LPEI and PAA. We determined that the charge characteristics of these polyelectrolyte chains can be precisely manipulated by application of an electric field. During electric-field-assisted LbL assembly, a positive bias was applied to facilitate anionic PAA adsorption, and a negative bias was applied to facilitate cationic LPEI adsorption. This allowed for highly accelerated polyelectrolyte deposition as compared to conventional dipping-based assembly. Further investigation of the interplay between the film growth behavior and the applied electric field revealed rather complex behaviors, with the film showing nonmonotonic growth depending on the pH conditions of LbL assembly. We attributed this nonmonotonic growth to competitive interactions between the electrolysis of water and the electrophoretic deposition of polyelectrolytes onto the electrode surface. By exploiting this phenomenon, we were able to successfully induce LbL assembly of LPEI/PAA even under pH conditions that cannot be used in the conventional dipping method. Moreover, by utilizing a patterned ITO substrate, we achieved patterned assembly of a polyelectrolyte multilayer using electric-field-assisted LbL assembly. Our results not only provide insight into electric-field-assisted LbL assembly of weakly charged polyelectrolytes but also indicate that LbL assembly free of pH constraint is feasible. Our method can potentially be used in various downstream applications such as the synthesis of hybrid biomaterials, the construction of biosensing platforms, and basic scientific research on charged polyelectrolytes.

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REFERENCES

(1) Hammond, P. T. *Adv. Mater.* **2004**, *16*, 1271.

(2) Lee, D.; Rubner, M. F.; Cohen, R. E. *Nano Lett.* **2006**, *6*, 2305.

(3) Martinez-Otero, A.; Evangelio, E.; Alibes, R.; Bourdelande, J. L.; Ruiz-Molina, D.; Busque, F.; Hernando, J. *Langmuir* **2008**, *24*, 2963.

(4) Lee, J. S.; Cho, J.; Lee, C.; Kim, I.; Park, J.; Kim, Y. M.; Shin, H.; Lee, J.; Caruso, F. *Nature Nanotechnol.* **2007**, *2*, 790.

(5) Wood, K. C.; Zacharia, N. S.; Schmidt, D. J.; Wrightman, S. N.; Andaya, B. J.; Hammond, P. T. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 2280.

(6) Lee, S. W.; Kim, B. S.; Chen, S.; Shao-Horn, Y.; Hammond, P. T. *J. Am. Chem. Soc.* **2009**, *131*, 671.

(7) Decher, G. *Science* **1997**, *277*, 1232.

(8) Hammond, P. T. *Curr. Opin. Colloid Interface Sci.* **1999**, *4* 430.

(9) Caruso, F.; Caruso, R. A.; Mohwald, H. *Science* **1998**, *282*, 1111.

(10) Tang, Z. Y.; Kotov, N. A.; Magonov, S.; Ozturk, B. *Nature Mater.* **2003**, *2*, 413.

(11) Yoo, P. J.; Nam, K. T.; Qi, J. F.; Lee, S. K.; Park, J.; Belcher, A. M.; Hammond, P. T. *Nature Mater.* **2006**, *5*, 234.

(12) Cho, J.; Char, K.; Hong, J. D.; Lee, K. B. *Adv. Mater.* **2001**, *13*, 1076.

(13) Lee, Y. M.; Park, D. K.; Choe, W. S.; Cho, S. M.; Han, G. Y.; Park, J.; Yoo, P. J. *J. Nanosci. Nanotechnol.* **2009**, *9*, 7467.

(14) Schlenoff, J. B.; Dubas, S. T. *Macromolecules* **2001**, *34*, 592.

(15) Zacharia, N. S.; DeLongchamp, D. M.; Modestino, M.; Hammond, P. T. *Macromolecules* **2007**, *40*, 1598.

(16) Picart, C.; Mutterer, J.; Richert, L.; Luo, Y.; Prestwich, G. D.; Schaaf, P.; Voegel, J. C.; Lavalle, P. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 12531.

(17) Lavalle, P.; Gergely, C.; Cuisinier, F. J. G.; Decher, G.; Schaaf, P.; Voegel, J. C.; Picart, C. *Macromolecules* **2002**, *35*, 4458.

(18) Garza, J. M.; Schaaf, P.; Muller, S.; Ball, V.; Stoltz, J. F.; Voegel, J. C.; Lavalle, P. *Langmuir* **2004**, *20*, 7298.

(19) Yoo, P. J.; Zacharia, N. S.; Doh, J.; Nam, K. T.; Belcher, A. M.; Hammond, P. T. *ACS Nano* **2008**, *2*, 561.

(20) Dubas, S. T.; Schlenoff, J. B. *Macromolecules* **1999**, *32*, 8153.

(21) Schlenoff, J. B.; Ly, H.; Li, M. *J. Am. Chem. Soc.* **1998**, *120*, 7626.

(22) Shiratori, S. S.; Rubner, M. F. *Macromolecules* **2000**, *33*, 4213.

(23) Choi, J.; Rubner, M. F. *Macromolecules* **2005**, *38*, 116.

(24) Zacharia, N. S.; Modestino, M.; Hammond, P. T. *Macromolecules* **2007**, *40*, 9523.

(25) Sui, Z. J.; Schlenoff, J. B. *Langmuir* **2004**, *20*, 6026.

(26) Ngankam, A. P.; Van Tassel, P. R. *Langmuir* **2005**, *21*, 5865.

(27) Zhang, P.; Qian, J. W.; Yang, Y.; An, Q. F.; Liu, X. Q.; Gui, Z. L. *J. Membr. Sci.* **2008**, *320*, 73.

(28) Ngankam, A. P.; Van Tassel, P. R. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 1140.

(29) Olsen, C.; Van Tassel, P. R. *J. Colloid Interface Sci.* **2009**, *329*, 222.

(30) Brusatori, M. A.; Tie, Y.; Van Tassel, P. R. *Langmuir* **2003**, *19*, 5089.

(31) Clark, S. L.; Hammond, P. T. *Langmuir* **2000**, *16*, 10206.

(32) Suh, K. Y.; Kim, Y. S.; Lee, H. H. *Adv. Mater.* **2001**, *13*, 1386.

(33) Heyderman, L. J.; Schift, H.; David, C.; Gobrecht, J.; Schweizer, T. *Microelectron. Eng.* **2000**, *54*, 229.

(34) Smits, R. G.; Koper, G. J. M.; Mandel, M. *J. Phys. Chem.* **1993**, *97*, 5745.

(35) Weyts, K. F.; Goethals, E. J. *Makromol. Chem., Rapid Commun.* **1989**, *10*, 299.

(36) DeLongchamp, D. M.; Hammond, P. T. *Chem. Mater.* **2003**, *15*, 1165.

(37) Veenhuis, R. B. H.; van der Wouden, E. J.; van Nieuwkasteele, J. W.; van den Berg, A.; Eijkel, J. C. T. *Lab Chip* **2009**, *9*, 3472.

(38) Zhao, J.; Zhang, R. *Atmos. Environ.* **2004**, *38*, 2177.

(39) de Souza, R. F.; Padilha, J. C.; Goncalves, R. S.; Rault-Berthelot, J. L. *Electrochem. Commun.* **2006**, *8*, 211.

(40) Guillaume-Gentil, O.; Graf, N.; Boulmedais, F.; Schaaf, P.; Vörös, J.; Zambelli, T. *Soft Matter* **2010**, *6*, 4246.

(41) Zhitomirsky, I. *Adv. Colloid Interface Sci.* **2002**, *97*, 279.

(42) Kuhn, A. T.; Chan, C. Y. *J. Appl. Electrochem.* **1983**, *13*, 189.

(43) Honda, T.; Murase, K.; Hirato, T.; Awakura, Y. *J. Appl. Electrochem.* **1998**, *28*, 617.

(44) Kershner, R. J.; Cima, M. J. *Electrochem. Soc. Proc.* **2002**, *21*, 1.

(45) Chao, C. I.; Chuang, K. R.; Chen, S. A. *Appl. Phys. Lett.* **1996**, *69*, 2894.

(46) Park, J. S.; Cho, S. M.; Han, G. Y.; Sim, S. J.; Park, J.; Yoo, P. J. *Langmuir* **2009**, *25*, 2575.

(47) Berg, M. C.; Yang, S. Y.; Hammond, P. T.; Rubner, M. F. *Langmuir* **2004**, *20*, 1362.