pH-Amplified Exponential Growth Multilayers: A Facile Method to Develop Hierarchical Micro- and Nanostructured Surfaces

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We report a direct method to amplify the exponential growth of multilayers significantly by the alternating deposition of polyethylenimine (PEI) at high pH and poly(acrylic acid) (PAA) at low pH. The alternating pH switches the degree of ionization of the polyelectrolytes in the multilayers, which enhances the diffusion of PEI into and out of the film and hence increases the deposited mass per cycle. The synergistic action of the pH-tunable charge density and diffusivity of the weak polyelectrolytes provides a new method for the enhanced growth of multilayers with hierarchical micro- and nanostructured surfaces.

Introduction

Biological hierarchical structures provide design criteria for functional micro- and nanostructured surfaces.1-3 Several methods including electrospinning, polymer phase separation, self-assembly, photolithography, and soft lithography can be used to fabricate these surfaces with specific properties.3-6 Most procedures involve complicated multistep processes and require a rigorously controlled environment, typically leading to high manufacturing costs. Layer-by-layer self-assembly (LBL) has been explored recently as a method to construct superhydrophobic coatings containing topographical features on the micro- and nanometer size scales.7-11 This method, which is based on the alternating deposition of oppositely charged polyelectrolytes, provides a simple, versatile, and robust tool for constructing ultrathin films with nanoscale topographical features. However, most layer-by-layer assembly processes are limited with respect to their ability to produce topographic features in the micro- and nanometer size ranges (hierarchical structures) simultaneously. Rubner and co-workers reported that when multilayer films made of weak polyelectrolytes (poly(allylamine hydrochloride) (PAH)/poly(acrylic acid) (PAA)) are immersed in a low-pH solution the pH of ionization of the polyelectrolytes in the multilayers, which enhances the diffusion of PEI into and out of the film during each deposition step. The diffusivity of the polyelectrolyte was found to correlate with the concentration of uncompensated polycation/polyanion charges within the multilayer. However, the growth of multilayers still exhibited relatively slow growth behavior up to a maximum thickness of 100 nm per bilayer. Rubner and co-workers reported on the effect of pH on the protonation of weak polyelectrolytes. They demonstrated that an alternate deposition of PAH at high pH and PAA at low pH increased the total thickness of the film for a given number of multilayers.13 However, because both commercially available PAA and PAH in their case do not diffuse easily, the multilayered films assembled at different pH values still exhibited typical linear growth behavior up to a maximum thickness of 140 nm for each bilayer.13,14 Lynn and co-workers13 have synthesized low-molecular-weight PAA, which can diffuse, and they found that this can result in exponential growth when assembled alternately with PAH. However, the thicknesses of the films is still limited to 562 nm for 10 bilayers. Recently, some of us reported the possibility of enhancing the exponential growth of multilayers by adding silver nitrate, which also induced

topographic features in films exhibiting micro- and nanostructures. 19

Here we demonstrate that a combination of the concepts described by the Strasbourg group 12-14 and by Rubner and coworkers18 enhances multilayer growth beyond that previously reported. Using the easily diffusing polyethyleneimine (PEI) and poly(acrylic acid) (PAA) as polyanions allows us to control the charge density via pH and results in the growth of films as thick as 3.25 μm after only seven deposition cycles. More importantly, this procedure also provides a controllable way to produce hierarchical micro- and nanostructured surfaces simultaneously.

Changing the pH allows us to tune the size range of the obtained morphologies. The topography of the multilayer structure can be fixed by thermal cross-linking and can be turned into a superhydrophobic surface by the chemical vapor deposition of (tridecafluorooctyl)-triethoxysilane.

Experimental Section

Materials. Poly(acrylic acid) (PAA, Mw = 100 000), polyethyleneimine (PEI, Mw = 25 000, water-free), and (tridecafluoro octyl)-triethoxysilane were obtained from Sigma-Aldrich and Degussa Company (Germany), respectively. FITC-labeled PEI was prepared by adding 5 mg of FITC succinimidy ester to 80 mL of 0.5% PEI aqueous solutions at 4 °C for 48 h. The free dyes were dialyzed in 0.05 M acetic acid aqueous solutions for 4 weeks.

Preparation of Polyelectrolyte Multilayer Thin Films. PEI/PAA multilayer films were constructed on 3-aminopropyltriethoxysilane (APTES)-coated glass slides using 1 mg mL−1 PEI and 3 mg mL−1 PAA aqueous solutions. The multilayer films were built by first immersing the substrate in the PAA solution for 15 min, followed by rinsing with pure water (with a pH of approximately 5.5) three times; the substrates were then immersed in PEI solution for 15 min, followed again by washing three times with pure water. The adsorption and washing steps were repeated until 15 layers were obtained. The multilayer films were thermally cross-linked at 180 °C for 2 h to preserve the surface morphology and to study their characteristics by SEM and AFM. Throughout the text, PAA/m/PEI/m is used to mean that multilayer films were constructed using PAA at pH m and PEI at pH n. For example, PAA5/PEI8 means that multilayer films were constructed with PAA at pH 5 and PEI at pH 8.

Preparation of Hydrophobic Surfaces. Very low surface energy surfaces were obtained by the chemical vapor deposition of (tridecafluorooctyl)-triethoxysilane. Together with (tridecafluoro octyl)-triethoxysilane, the multilayers films were sealed in a chamber and placed in an oven at 130 °C for 2.5 h. Then, the samples were withdrawn from the chamber and placed in an oven at 180 °C for 1.5 h to remove all unreacted silane molecules.

Characterization. QCM measurements of dried multilayer films were performed with a KSV QCM-Z500 quartz resonator with both sides coated with Ag (F0 = 9 MHz). Confocal laser scanning microscopy (CLSM) investigations were carried out with a Zeiss Axiosvert 200 microscope equipped with a Bio-Rad Radiance 2100 confocal system using a ×40/1.4 oil-immersion objective and 0.4 μm z-section intervals. The multilayered films for the CLSM investigation were constructed on glass slides as described above, the only difference being that the FITC-labeled PEI replaced nonlabeled PEI in the 16th deposition layer. FITC fluorescence was detected after excitation at 488 nm with a cutoff dichroic mirror (488 nm) and an emission band-pass filter from 505 to 530 nm (green). To image the whole film, consecutive z sections were collected at 0.4 μm intervals. Vertical sections were calculated, and the film thicknesses were determined. A field-emission scanning electron microscope (FESEM; FEI, Sirion 100) and an atomic force microscope (SPA 400, Seiko Instrument, Inc.) in tapping mode were used to measure the surface morphology and to determine the rms roughness of the multilayer films. Sessile drop contact angles (CA)

Figure 1. (a) QCM frequency shifts of multilayer films assembled at pH PAA7.2/PEI7.2 ( ), PAA5/PEI8 ( ), and PAA2.85/PEI9 ( ). (b) Thickness of the multilayer films prepared at pH PAA2.85/PEI9 as determined by SEM of the film cross sections.

Results and Discussion

The polyelectrolyte multilayers were constructed by the alternate deposition of PEI at high pH and PAA at low pH. To quantify the effect of pH on the growth rate of the multilayers, the increases in film mass and thickness were monitored by QCM and SEM at different pH values. Figure 1 shows the amplification of film growth with increasing pH difference of the dipping solution as measured by the film mass and its thickness. Films prepared at pH 7.2 for both PEI and PAA grow, as expected, linearly with the number of depositions. A nonlinear increase in mass and thickness is observed when the multilayers are prepared at PEI 8.0/PAA 5.0. The nonlinearity in film growth becomes more pronounced with increasing pH difference. A film of 3.25 μm thickness (as measured by SEM) was obtained after seven deposition cycles with PEI at pH 9 and PAA at pH 2.85. PAA7.2/PEI7.2 multilayer films remained transparent for up to eight bilayers; PAA5/PEI8 multilayer films became semitransparent at about five bilayers; and PAA2.85/PEI9 multilayer films became nontransparent at about four bilayers when PAA was the outermost layer.

The buildup of the multilayers was also monitored by confocal laser scanning microscopy (CLSM) by adding fluorescently labeled PEI (PEI*). Figure 2a shows a vertical section through a (PAA/PEI) film containing a labeled PEI–FITC outermost layer. The green fluorescent zone represents a large, continuous nontransparent at about four bilayers when PAA was the outermost layer.

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For all of the multilayer films, PEI FITC can diffuse out of the film. Thus, the exponential growth mechanism of the multilayer films relies on the diffusion of PEI molecules into and out of the multilayer films during each deposition cycle. Both polyethylenimine (PEI) and poly(acrylic acid) (PAA) are weak polyelectrolytes whose charge density can be changed by the pH of the solution. The alternating exposure of the complete film structure at high pH (in PEI solution) and low pH (in PAA solution) enhances the concentration of uncompensated for polycations/polyanions within the multilayer (Scheme 1). Hence, the PEI in the high-pH dipping solution not only will compensate for the countercharges in the surface layer but also will diffuse into the film to compensate for the bulk charges. When the multilayer is further brought in contact with PAA at low pH, the protonated PEI with uncompensated bulk charges will diffuse out to the interface to be neutralized. Because the pH will affect the charge density in the complete film structure, the amount of uncompensated for polyelectrolyte is controlled by the concentration of uncompensated for bulk charges, which is proportional to the total thickness of the film. The synergetic action of the pH-tunable charge density and diffusivity of the weak polyelectrolytes causes accelerated multilayer growth.

IRAS-FTIR was used to measure the degree of ionization of carboxyl groups of PAA molecules in the multilayer films. Two adsorption bands of the carboxylic acid functional groups of PAA were considered: \( \nu = 1565-1542 \text{ cm}^{-1} \) (asymmetric stretching band of COO\(^-\)) and \( \nu =1710-1700 \text{ cm}^{-1} \) (C=O stretching of COOH). Deconvolution of the vibrational bands was carried out with Microcal Origin software assuming a Gaussian band shape. The degree of ionization of PAA (R) at a given pH was calculated from \( R = [A(COO^-)]/[A(COOH) + A(COO^-)] \times 100(\%) \), where A is the area under the bands. For the PAA/PEI multilayer films constructed at pH 7.2, the degree of ionization of carboxyl groups of PAA in the multilayers remains constant with the number of adsorption steps. However, when the multilayer films are constructed with PAA at pH 5 and PEI at pH 8, the degree of ionization of carboxyl groups of PAA alternates between 73% (PAA as the outermost layer) and 88% (PEI as the outermost layer). Upon increasing the pH difference of the dipping solutions, the effect of adsorption steps on the ionization of the carboxylic acid residues becomes more pronounced (e.g., for PAA2.85/PEI9, it alternates between 35 and 91%).

To test the hypothesis that the amount of polyelectrolyte diffusion into and out of the film and hence the resulting incremental film thickness increase are proportional to the concentration of uncompensated for charge in the film, we fitted the QCM data for film growth to the expression \( y = a \exp(bx) + c \), where \( y \) is the measured frequency shift after \( x \) deposition cycles, \( a \) is the point at which steep growth is initiated, and \( b \) is the rate of film growth. The values of exponent \( b \) were plotted against the difference in the degree of ionization of the multilayers assembled at different pH value (Figure 3). The linear relationship supports our model because it demonstrates that the growth rate (or incremental thickness increase) of the PAA/PEI multilayers is proportional to the degree of ionization of the bulk polyelectrolyte.
The multilayered films were thermally cross-linked (by heat-induced amide formation of the carboxylate–ammonium complexes) to preserve the surface morphological features. Both scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to examine the topography of the multilayered films constructed at different pH pairs. Not shown here are the SEM data before thermal treatment, but they closely resemble those recorded after thermal cross-linking. A progressive increase in the roughness of the films is observed with increasing pH difference of the dipping solutions. Films prepared at pH 7.2 are flat and featureless with a slight granular structure (Figure 4a). A more globular structure emerges in the multilayer films prepared at PEI 8.0/PAI 5.0 (Figure 4b). The multilayer films constructed at PAA 2.85/PEI 9 exhibit distinct features on the micro- and nanometer length scales (i.e., vermiculate patterns of 500–1500 nm and micropores on the order of 10 µm (Figure 4c)). A magnification of the vermiculate patterns shows nanowrinkles of 100–200 nm (Figure 4d). The rms roughnesses of the multilayers prepared at 7.2/7.2, 8.0/5.0, and 2.85/9 are 23, 144, and 1329, respectively.

For the rough surface of the PAA2.85/PEI9 multilayer, the water contact angle is very close to zero before cross-linking. However, the water contact angle of the multilayer after heat cross-linking treatment is about 110° because of the formation of hydrophobic amide groups and the surface roughness. The rough surfaces were further modified by the chemical vapor deposition of (tridecafluorooctyl)-triethoxysilane to render them more hydrophobic. The thickness of the (tridecafluorooctyl)-triethoxysilane layer after cross-linking is about 2.5 nm according to the XPS measurement. The contact angle reaches 168° on the multilayer films constructed at 2.85/9, and the sliding angle becomes as small as 8°.

**Conclusions**

We demonstrated an easy, efficient method to amplify the growth of polyelectrolyte multilayers via the alternating deposition of PEI at high and PAA at low pH. The alternating pH switches the degree of ionization of the polyelectrolytes in the multilayers, which enhances their diffusion into and out of the film and hence increases the deposited mass per cycle. The synergetic action of the pH-dependent tunable charge density and diffusivity of the weak polyelectrolytes provides a new method for the enhanced growth of multilayers with hierarchical micro- and nanostructured surfaces. Therefore, surfaces exhibiting tunable topographic features in both the micro and nanometer size ranges can be achieved in only seven alternate deposition cycles of PEI and PAA. The topography of the multilayer structure can be fixed by thermal cross-linking and can be turned into a superhydrophobic surface by the chemical vapor deposition of (tridecafluorooctyl)-triethoxysilane. Compared to the previously described methods involving the addition of silver ions to enhance film growth, the described pH-modulation approach is simple and versatile. The strategy of LBL assembly at alternating pH, which deposits a diffusible weak polycation at high pH and a weak polyanion at low pH, provides a new route to the rapid, easy fabrication of multilayers with hierarchical topographic features.

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