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Surface Induced Porous Morphological Transition of the Organic Self-Assembled Monolayer Hybridized Polyelectrolyte Thin Films

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Introduction

Surface coating is used for materials to achieve a desired surface property without changing the whole material. Polyelectrolyte multilayer (PEM) deposition may be one of the most versatile techniques to create conformal surface coating in large area with a great control over the film thickness in nano-meter scale.[1,2] These multilayer films are assembled through, so called, the layer-by-layer (LbL) deposition process which is the repetitive, sequential dipping of the substrate into the oppositely charged polyelectrolytes solutions.[2] PEM films can be used for various substrates (glass slides, silicon wafer, plastics, *etc.*) without any difficult treatment.[3,4] Moreover, the functional groups which remained reactive after the film deposition allow further chemical reactions such as the polymer micro-contact printing and the selective crosslinking.[5] Due to these advantages, many studies using the LbL technique have conducted intensively to create functional coatings for electro-optical[6-9] and biomedical applications.[10-13] Other frequently used method of surface coating is self-assembled monolayer (SAM) formation. SAM can form organic interfaces with the properties largely controlled by the end groups of the molecules comprising of the film.[14-19] Certainly, these two methods are the most competitive fabrication techniques of surface coating. While the surface properties of most SAMs are presented by the nature of the end groups of SAM molecules, PEM films exhibit their surface properties that are orchestrated by the chemical compositions of the polyelectrolyte film and physical factors such as surface morphology, thickness, *etc.*. If these two very different materials meet, what phenomena will occur at the interface? How would they compensate their discrepancy?

In this paper, we present a study of the coating system that was fabricated as a mixture of PEM and SAM. The hybrid films were prepared by polyelectrolyte multilayers comprised of hydrophilic polyelectrolytes assembled atop of hydrophobic SAM films. We have observed a unique phase separation of the SAM/PEM hybrid film, which lead the formation of nano-pores of the film surface. Surface properties including wetting and biological interaction behaviors of the hybrid films are also discussed in this paper.

Results and Discussion

We created a hybridized coating system of a hydrophilic polyelectrolyte multilayer (PEM) and a hydrophobic low-molecular organic layer by layer-by-layer deposition of polyelectrolytes over a self-assembled monolayer (SAM)-coated silica substrate. Poly(acrylic acid) (PAA) and poly(acrylamide) (PAAm) were used for the polyelectrolyte multilayers with hydrogen bonding interactions. For the organic monolayer, trimethoxy silane compounds with phenyl, octyl and amine terminal groups were used.

Figure 1 illustrates the process of the hybridized SAM/PEM films. A cleaned substrate was immersed into a 1 mM phenyl trimethoxy silane dissolved in toluene solution under dry N_2 gas. The trimethoxy-silyl groups in this molecule could readily bind to the silica surface *via* condensation of hydroxyl groups of silane therefore, the phenyl group on the other side of molecule would represent as a new outermost surface. After 12 h of reaction, the substrate was removed from the reaction bath, exhaustively washed with dry toluene and then ultrasonicated in toluene for 10 min. Then the film was treated at 120 °C for 2 h to crosslink any unreacted

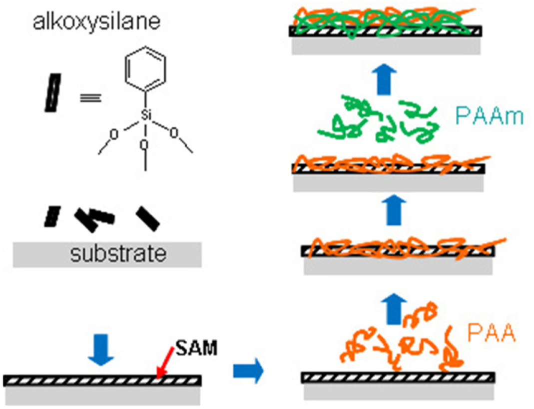

Figure 1. Schematic explanation of the procedure to form hybridized polyelectrolyte multilayers on atop of hydrophobic organic silane monolayer film.

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silane group during the deposition. This monolayer-coated substrate was kept under N_2 gas until the PEM deposition process was performed.

The SAM-coated substrates were first immersed into a poly(allylamine hydrochloride) (PAH) solution (0.01 M, pH 3.0) for 15 min followed by rinsing with pH 3.0 water. This step introduces a primer/adhesion layer for the subsequently deposited PAA and PAAm layers. The detailed study of the formation of PAA/PAAm multilayer film can be found in previous work.[5] Although the adhesion of the PEM layers onto the SAM surface was somewhat enhanced in the case of a PAH layer was used, similar results were obtained without this primer layer. The substrates were then dipped into PAA solution followed by three rinse steps (2, 2, 1 minute in separate bins) and then dipped into a PAAm solution followed by the same rinsing procedure. Deposition of a PAA layer and a PAAm layer completes one cycle, which is referred as a single bilayer formation. This dipping cycle was repeated until the multilayer was produced. The deposited multilayer films were thermally crosslinked at 90 ºC under vacuum for 8 h. Details concerning the layer-by-layer assembly and crosslinking of PAA/PAAm PEM can be found in the previous literature.[10]

Tapping mode AFM images were obtained from the PEM films with the bilayer numbers varying in the range of 1~4 (one PEM bilayer consists of a pair of PAA and PAAm deposition). The height contrast AFM images of the phenyltrimethoxy-silane monolayer (herein designated as SAM) and the PEM film coated over the SAM monolayer [hereafter, SAM/$(PEM)_n$, where n is the number of bilayers], are presented in Figure 2.

The phenyl trimethoxy silane-coated surface exhibited very smooth morphology, resulted from a close-packed self-assembled monolayer, shown in AFM image (Figure 2(a)). In Figure 2(b), as a sharp contrast, the PEM film with a 1.5 bilayers deposited on the SAM-coated substrate shows nanoporous morphology. Interestingly, SAM/$(PEM)_{1.5}$ film was constructed with the same thicknesses of PEM and SAM films (about 2 nm for each unit). This porous structure of the film disappeared when the thicker PEM films were deposited atop of the SAM-coated surface. It seems the nanoporous morphological transition of the hybrid film only occurs when the PEM and SAM film thicknesses are about the same. We tested a couple of other hydrophobic SAM coatings than phenyl-silyl compound for SAM/PEM system. However, any distinctive morphological change was not observed with other cases. The reason why phenyl-end group shows the most dramatic change on surface morphology is not clear yet, but may be the most hydrophobic nature among the organic SAMs used in this study would play some role in this micro-phase separation. A further study will be followed.

Notably, all the SAM/PEM films and SAM-only film in Figure 2 were thermally treated. In the case of SAM, thermal crosslinking of silane is a general procedure to stabilize unbound silane groups. For the PEM or SAM/PEM hybrid film, this cross-linking reaction was required for the further investigation under high pH condition because the PEM film assembled by H-bonding might be dissolved at such environment. So, we checked morphological change of the PEM film by thermal annealing in the absence of the SAM coating. After thermal stabilization reaction, surface of the PEM film seemed to undergo a slight densification, but any other morphological change was not observed. Therefore, the porous morphology of the SAM/PEM film was induced by the interactions of the PEM film with the hydrophobic SAM film, not only by thermal shrinkage.

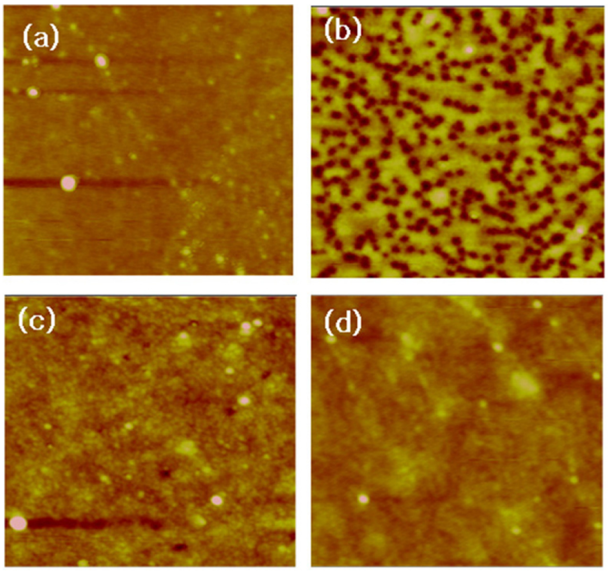

Figure 2. Height contrast AFM images of the SAM and SAM/$(PEM)_n$ coating on SiO_2/Si substrate. AFM images of (a) a phenyl-terminal silane self-assembled monolayer (SAM) (b) SAM/$(PEM)_{1.5}$, (c) SAM/$(PEM)_2$, (d) SAM/$(PEM)_{3.5}$. All PEM films were thermally cured at 90 ºC for 8 h. All images are taken with the size of 1×1 μm^2.

Contact angle measurements were performed with de-ionized water droplets by contact angle analyzer. The hydrophobic nature of the phenyl-terminated SAM is resulted as a high contact angle (~75°) while hydrophilic PAA/PAAm (PEM) film (PEM only in Figure 3) showed relatively low contact angle value, ~38°. The high surface contact angle of SAM film became lower as more layers of the PEM film was deposited atop of the SAM layer. As shown in Figure 3, the surface contact angle of the SAM/PEM film was readily lowered to ~40°. Actually, the contact angle of the blended film of SAM and PEM film was obtained as the lowest, when the bilayers of PEM film were only 1.5. This PEM layer coincides with the film which reveals the nanoporous morphology.

This high wettability obtained from the hybrid film after porous transition brought a dramatic change in the non-spe-

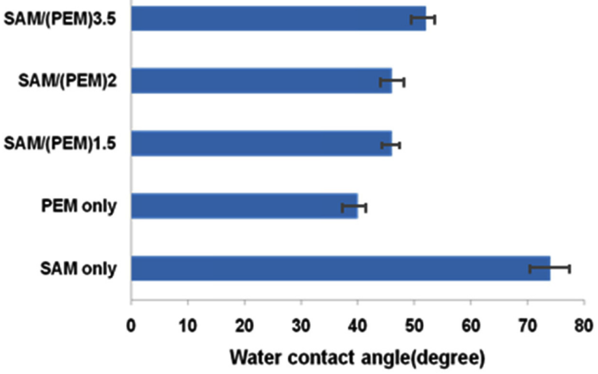

Figure 3. Water contact angles of the SAM/PEM films as compared with those of SAM or PEM only coating on SiO_2/Si substrate.

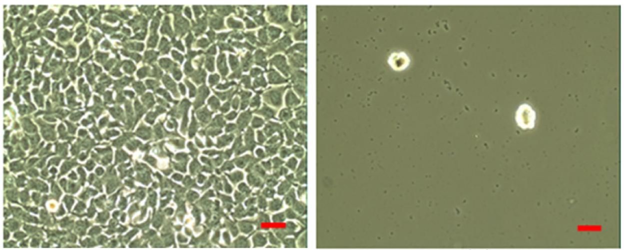
(a) (b)

Figure 4. Phase contrast optical microscope images of HEK293 cells on (a) SAM only and (b) SAM/$(PEM)_{1.5}$ films.

cific adhesion of cells onto the film (Figure 4). We observed excellent blocking capability of the nano-porous film toward 293 HEK cells. These cells are originally surface-adhesive cells as shown in Figure 4(a) where the SAM only film was used.

This result is in a good agreement with our previous study of nano-porous PEM films on cellular interactions.[20] The PEM film exhibited excellent prevention of non-specific cell-adhesion when the film morphology was changed from non-porous to nano-porous structure. These results suggest that surface morphology may be an important factor to control cellular adhesion onto the surface.

In conclusion, we have studied the hybrid coating system that was comprised of the different characteristics such as hydrophobic versus hydrophilic and low molecular organic versus polymeric compound. The hybrid films were prepared by PEM and SAM. When the film thicknesses of SAM and PEM layers became equivalent, there was a nanoporous morphology appeared by micro-phase separation. This morphological change only occurs at the certain thickness, and affects the surface wettability as well as biological property. We expect this peculiar morphological transition between two distinctive layers may be a clue to understand dynamic interfacial systems existing in nature.

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