

Hydrogen-bonding based multilayer assemblies by self-deposition of dendrimer

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We reported on hydrogen-bonding directed Layer-by-Layer assemblies by self-deposition of a kind of dendrimer bearing carboxyl groups on its periphery that act as hydrogen bonding donor as well as hydrogen bonding acceptor.

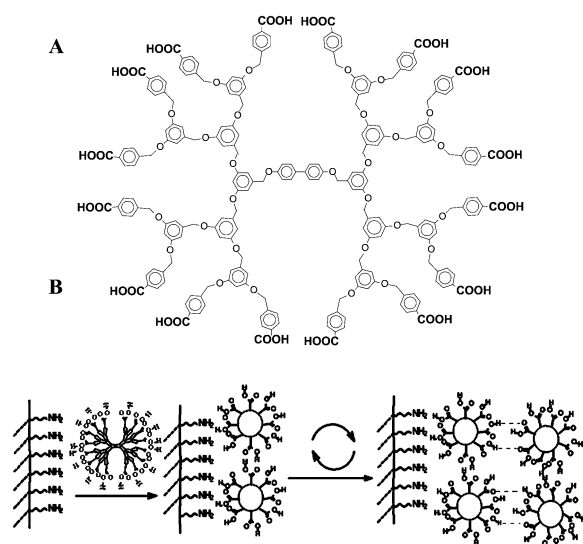
The fabrication of structurally regulated ultrathin organic films by simple and convenient methods has gained a lot of attention in the modern material science.¹ The alternating adsorption of oppositely charged polyelectrolytes introduced first by G. Decher,² has proved to be a powerful and versatile method to fabricate multicomposite assemblies. The driving force for the multilayer buildup is based on the electrostatic interaction of the complementary cation–anion pairs formed at the liquid–solid interface. Actually, many other strong or weak molecular interactions can be applied in the layer-by-layer assembly, such as coordination bonding,³ hydrogen bonding,⁴ charge-transfer interaction,⁵ specific recognition and so on.⁶ In general, the interaction between building blocks, which are used to form the multilayer film, is complementary. Usually regarding multilayer fabrication, the building blocks were two different kinds of molecules in each film system. Therefore, the study of using the same molecule to fabricate a multilayer film will certainly enrich field of the layer-by-layer assembly.

In this paper, we report on the hydrogen-bonding based multilayer assemblies by self-deposition of a dendrimer. The term “self-deposition” is employed because this multilayer fabrication uses only one type of molecule as building block, carboxyl-terminated poly-ether dendrimer (dendrimer-COOH, Scheme 1A). In this system the dendrimer-COOH is the hydrogen bond donor as well as the hydrogen bond acceptor. Previous studies show that the driving force from a single

hydrogen-bonded pair needs amplification to produce an integral film.⁴ Dendrimers possess a unique surface of multiple chain ends and the number of surface groups can be precisely controlled as a function of synthetic generations. We envisage that dendrimer-COOH with high-density surface carboxyl groups makes it possible to provide enough hydrogen-bonded pairs.

The dendrimer-COOH was used as a building block for the construction of a self-deposition multilayer, which was synthesized according to literature.⁷ Quartz was modified with 3-aminopropyl (triethoxysilane) in advance for UV-Vis measurement, resulting in a NH₂-tailed surface.⁸ CaF₂ substrate was modified with PEI in advance for transmission FT-IR measurement. Gold covered glass was modified with 3-mercapto-propionic acid in advance for reflection FTIR. The construction of the multilayer films is schematically shown in Scheme 1B and described as follows. The 3-aminopropyl silanized substrate was first immersed in a dendrimer/methanol solution for 2 mins, after washing with methanol and drying with nitrogen, the substrate covered with dendrimer-COOH was again dipped into the solution for 2 mins to get another dendrimer layer. A multilayer film could be obtained by repeating the above steps in a cyclic fashion. Two minutes assembly time ensures that the deposition of dendrimer-COOH reaches saturation. Kinetics studies show that after 20 s assembly the deposition saturates.

Ultraviolet visible (UV-Vis) absorption spectroscopy was used to follow the assembly process of the dendrimer multilayer films. Fig. 1A shows the UV-Vis absorption spectra of the multilayer films of dendrimer-COOH with a different number



Scheme 1 (A) The structure of carboxyl-terminated polyether dendrimer. (B) The schematic representation of the construction of dendrimer multilayer films.

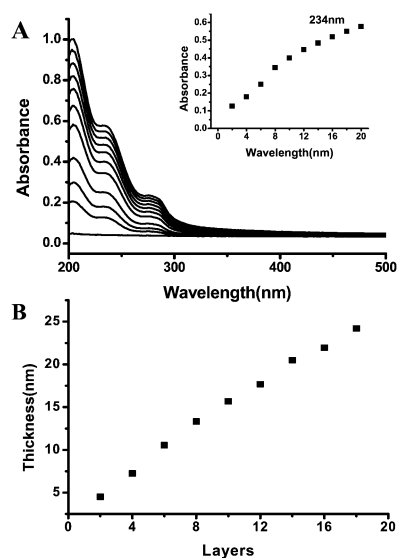


Fig. 1 (A) UV-Vis spectra of the alternating multilayer film of dendrimer-COOH with an increasing number of layers. (Concentration of dendrimer in methanol: 4 mg/25 ml; assembly time: 2min/layer). (B) the thickness of the self-deposition film estimated by ellipsometry.

of layers on a quartz slide. The absorption band at 234 nm in the UV region is assigned to the dendrimer. The linear increase of the optical density at 234 nm of the films with increasing number of layers indicates a process of uniform assembly. The uniform self-deposition of dendrimer has been also confirmed by ellipsometry as shown in Fig. 1B. The ellipsometry data indicate the thickness of each layer as approximately 2 nm. AFM was used to observe the surface of 1-layer dendrimer-COOH self-deposition film. The roughness (RMS) was calculated to be 0.7 nm.

Infrared reflection-absorption and transmission spectroscopy were used to study the dendrimer's structure in a self-deposition multilayered film. In thin layers, band intensities depended on the orientation of the transition dipole moment (TDM) associated with the vibration and the electric field direction at the substrate surface. The well-known metal surface selection rule states that only vibration with TDM components perpendicular to the plane of the substrate are observed.⁹ Fig 2 shows that the intensity of carbonyl group vibration (1697.0 cm^{-1}) is higher in the reflection spectrum than in the transmission spectrum. According to the metal surface selection rule, the carboxyl group preferred vertical orientation to the gold surface. In the cast film of dendrimer-COOH, the intensity of carbonyl group has no apparent difference between the reflection spectrum and transmitted spectrum. Furthermore, carbonyl group C=O vibration, which appears at 1697.0 cm^{-1} , is much lower than the normal stretching band of free carbonyl group peaks around 1720 cm^{-1} . The low shift of the wave number is indicative of formation of hydrogen bonding between the carboxyl groups. In addition, it was found that the self-deposition of dendrimer is pH sensitive. The self-deposition multilayer film can be destroyed by strongly alkaline solution ($\text{pH} > 9$) or acidic solution ($\text{pH} < 5$). This is a further proof that hydrogen-bonding plays an important role in the multilayer fabrication.

The effect of the concentration of dendrimer in methanol on the film assembly by self-deposition has been studied. Fig. 3 shows the absorbance of the film versus the number of layers deposited, when we performed the repetition of deposition from dendrimer solution at various dendrimer concentrations. The

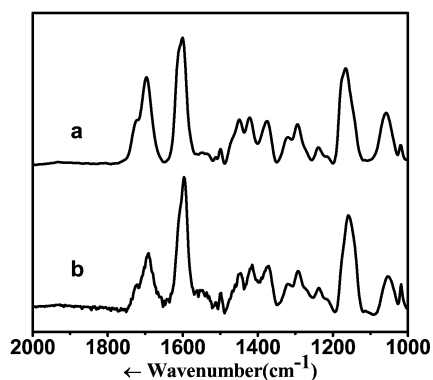


Fig. 2 Infrared reflection absorbance spectrum (a) and infrared transmitted absorbance spectrum (b) of the alternating multilayer film of dendrimer-COOH (10 layers).

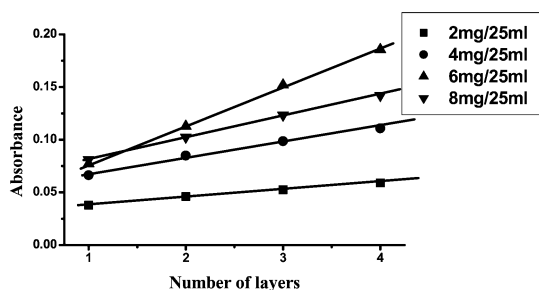


Fig. 3 UV-Vis spectra of the alternating multilayer film of dendrimer with different concentration of dendrimer in methanol.

stepwise absorbance was observed with increasing number of cycles in all cases, indicating the stepwise assembly of dendrimer films on the substrate. For low concentration, the amount of dendrimer deposited at each layer increases with the concentration. However, for concentration higher than $6\text{ mg}/25\text{ mL}$ the amount of dendrimer deposited at each layer decreases. We speculate that the dendrimer-COOHs in the solution interact with the molecules at the outmost layer through hydrogen bonding. This interaction can draw the dendrimer-COOHs at the layer back into the solution and for higher concentration it is sufficiently strong to affect the self-deposition process. So there should be a balance of deposition and desorption for the layer buildup.

Does the drying process play an important role in the self-deposition process? In order to clarify this, we fabricated the self-deposition multilayer without the drying process. First, 3 layers were deposited onto the substrate to prove that the experiment works as usual. Thereafter, the substrate was dipped into the solution of dendrimer for 2 mins, and then rinsed with methanol without drying. At this stage there should be 4 layers on the substrate. The substrate was dipped into the solution for 2 mins again. If drying has an effect, then the fifth layer could not be fabricated because after the fourth layer the substrate was not treated with the drying process. However, UV-Vis data showed that the film has 5 layers and we concluded that the dryness process has no effect on the self-deposition.

In conclusion, an ultrathin multilayered film was fabricated using one kind of molecule, dendrimer-COOH, by a self-assembly technique. The experiments show that the dendrimer-COOH assembly is a continuous and uniform adsorption process. The layer buildup is based on an equilibrium between deposition and desorption and depend on the dendrimer concentration. Comparative data from infrared reflection and transmission spectra indicate the rearrangement of dendrimer-COOH after deposition on the solid substrate, which may facilitate the formation of hydrogen bonding for stabilizing the multilayer. This research will enrich the field of the layer-by-layer assembly.

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