



Fabrication of free-standing polyelectrolyte multilayer films: A method using polysulfobetaine-containing films as sacrificial layers

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ABSTRACT

A new pH-dependent sacrificial system based on zwitterionic polysulfobetaine was proposed for the fabrication of free-standing polyelectrolyte multilayer films. The zwitterionic polysulfobetaine, poly(4-vinylpyridine propylsulfobetaine) (P4VPPS), was synthesized and its layer-by-layer (LbL) self-assembly behavior with poly(diallyldimethylammonium) (PDDA) as counterpart was investigated by using UV–vis absorption spectroscopy, quartz crystal microbalance (QCM) and atomic force microscopy (AFM). The LbL multilayer films of PDDA/P4VPPS were successfully constructed in acid aqueous solution at pH 2 with 0.5 M NaCl. The resultant PDDA/P4VPPS multilayer films were pH-dependent and could be disintegrated in alkali aqueous solutions, especially with $\text{pH} \geq 12$. This disintegration property rendered such multilayer film as a sacrificial layer for further preparing free-standing polyelectrolyte multilayer films. The PDDA/poly(sodium 4-styrenesulfonate) (PSS) multilayer films deposited on the PDDA/P4VPPS sacrificial layer were confirmed to be successfully released after treated successively by alkali aqueous solution at pH 12 and ethanol. The obtained PDDA/PSS free-standing multilayer films had thicknesses of ca. 847 nm.

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1. Introduction

The layer-by-layer (LbL) self-assembly technique has received wide attention and emerged as a versatile and convenient method for the construction of ultra thin multilayer films with well-defined architecture at the nanometer level and well-controlled chemical composition [1,2]. The prepared multilayer films possess much potential application in separation membranes, sensors, optical and electronic film devices, biological templates and so forth [3–15]. Generally, the film is tightly bound to its substrates (quartz slides, silicon wafers and supporting film, etc.). However, substrates are usually needless in the study of bulk properties and applications of LbL multilayer films [10,16]. Thus, the fabrication of multilayer films without substrate, i.e. free-standing LbL multilayer film, is of great significance.

Up to now, there are several methods for the fabrication of free-standing LbL multilayer films, such as, dissolving substrates [17–19], peeling directly LbL multilayer films from a low-surface energy surface [10,16], dissolving the sacrificial layer between the substrate and the LbL multilayer film [20–23], and so on [24]. However, the most commonly used method is dissolving the “sacrificial layers” due to its simple fabrication and extensive choice of

different types of LbL multilayer films. Usually, the sacrificial layer can be either a spin-coated film, spray polymeric film and LbL self-assembled multilayer film. Jiang et al. prepared the free suspended gold nanoparticle array using cellulose acetate (CA) spin layer coated on the freshly cleaned silicon substrate as the sacrificial layer [21,22]. Decher et al. reported that the free-standing PAH/PSS multilayer films were prepared and released at physiological conditions using hydrogen-bonded PAA/poly(ethyleneglycol) (PEG) multilayer films as sacrificial layer [20]. Schlenoff et al. reported the fabrication of free-standing PDDA/PSS multilayer film with PDDA/PAA LbL multilayer films as sacrificial layer, which can be decomposed in aqueous solutions with high salt concentration [23].

However, to the best of our knowledge, little attention was paid on the usage of pH-dependent LbL multilayer film formed by the electrostatic interaction as a sacrificial layer in the fabrication of polyelectrolyte free-standing LbL multilayer films. Until recently, the LbL self-assembly of pH-dependent multilayer films formed by the electrostatic force was reported [25,26]. Schlenoff et al. prepared LbL multilayer films of poly(2-vinylpyridine propylsulfobetaine) (P2VPPS) with PSS or PAA at low pH ($\text{pH} < 1$) [25]. Kharlampieva et al. reported the electrostatic LbL self-assembly of poly(carboxybetaine)s (PCB) with poly(sodium 4-styrenesulfonate) (PSS) and the disintegration of PCB/PSS multilayer films at pH 7.2 [26,27]. The disintegration of pH-dependent LbL multilayer

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films at various pH conditions makes them potential candidates as the sacrificial layers. The successful application of such pH-dependent sacrificial layers might broaden the choice of polyelectrolytes for fabricating different types of free-standing films.

In the present work, a zwitterionic polysulfobetaine, poly(4-vinylpyridine propylsulfobetaine) (P4VPPS), was synthesized to fabricate LbL multilayer films with PDDA. The disintegration of the resultant PDDA/P4VPPS multilayer films was investigated and found that PDDA/P4VPPS multilayer films could be disintegrated in alkali aqueous solutions, especially with $\text{pH} \geq 12$. The PDDA/poly(sodium 4-styrenesulfonate) (PSS) LbL multilayer films deposited on the sacrificial layer of PDDA/P4VPPS films could be successfully released in alkali aqueous solution at pH 12 and the PDDA/PSS free-standing multilayer films were obtained in the air after treated by ethanol.

2. Materials and methods

2.1. Chemical and materials

Poly (dimethyldiallylammonium chloride) (PDDA) ($M_w = 100,000\text{--}200,000$ g/mol, 20 wt.% aqueous solution), poly(sodium 4-styrenesulfonate) (PSS, $M_w = 70,000$ g/mol), 1,3-cyclopropane-sultone (1,3-PS) and 4-vinylpyridine (4-VP) was purchased from Aldrich. Deionized water with a resistance of ~ 18 M Ω cm was used in all experiments. All experiments were carried out at 25 °C unless otherwise stated.

2.2. Synthesis of 4-VPPS monomer and P4VPPS

According to the method report by Monroy Soto et al. and our previous work [28–30], 4-vinylpyridine propylsulfobetaine (4-VPPS) was synthesized by the ring opening reaction of 1,3-PS with 4-VP. 0.11 mol of 1,3-PS was added to a solution of 0.1 mol of 4-VPPS in benzene in the presence of 6×10^{-4} mole of 1,3-dinitrobenzene, which was heated at 80 °C for 20 h under continuous stirring. The 4-VPPS was recovered as a white precipitate by filtration, washed thoroughly with acetone and dried under vacuum at 50 °C. The 4-VPPS was obtained in ca. 90% yield.

The poly(4-vinylpyridine propylsulfobetaine) (P4VPPS) was synthesized via free radical copolymerization in NaCl solution under nitrogen at 30 °C. Potassium persulfate and sodium bisulfite (mass ratio of $\text{K}_2\text{S}_2\text{O}_8$ $\text{NaHSO}_3 = 2:1$) were used as the initiator. For example, 3 g of 4-VPPS were dissolved in 12.5 mL of 0.5 mol/L NaCl solution. The reaction mixture was then kept at 30 ± 0.2 °C and purged with nitrogen for 20 min. Afterward, the reaction was initiated with $\text{K}_2\text{S}_2\text{O}_8$ and NaHSO_3 and allowed to continue for 8 h. The products were precipitated in acetone and further purified by repeated dissolution in water and precipitation in acetone. The precipitates were dried in a vacuum oven at 50 °C to constant weight. The intrinsic viscosity of the synthesized P4VPPS in 0.5 M NaCl aqueous solution at 30 °C was 118.4 mL/g. FT-IR spectrum of P4VPPS was recorded with Vector-22 FT-IR spectrometer (Bruker Company, Germany) by dispersing the sample in

KBr pellets. The chemical structure of the P4VPPS together with the PDDA and PSS used in this study are given in Fig. 1.

2.3. Fabrication and disintegration of PDDA/P4VPPS multilayer films

P4VPPS and PDDA were dissolved in acidic aqueous solution with pH 2 and 0.5 M NaCl to give a concentration of 2 mg/mL. The multilayer films were deposited on quartz slides by alternately dipping the substrates into the solutions of PDDA and P4VPPS at 25 °C for 10 min followed by two rinsing steps with 0.01 M HCl aqueous solution (pH 2) for 60 s each. The quartz slides were cleaned with freshly prepared piranha solution (3:7 mixture of 30% H_2O_2 and concentrated H_2SO_4) for 30 min followed by thoroughly rinsing with deionized water and drying with nitrogen prior to use. (Caution! Piranha solution is a very strong oxidizing agent and reacts violently with organic compounds. It should be handled with extreme care.) The multilayer films were dried with nitrogen prior to further experiment. The first layer was always PDDA layer and each bilayer consists of PDDA layer and P4VPPS layer. For example, a $(\text{PDDA}/\text{P4VPPS})_{10}$ multilayer film contains 10 bilayers of PDDA/P4VPPS. The dipping steps were repeated until the desired number of bilayers was achieved.

The disintegration of PDDA/P4VPPS multilayer film was performed in alkali solutions. A PDDA/P4VPPS multilayer film deposited on gold-polished AT-cut quartz crystal was sequentially immersed in alkali solution from pH 7 to 14 each for 30 min. Note that the total film thickness of $(\text{PDDA}/\text{P4VPPS})_{10}$ was measured by QCM before the disintegration test. Afterward, the quartz crystal was taken out and dried with nitrogen. The film thickness was re-measured by QCM.

2.4. Fabrication of free-standing PDDA/PSS multilayer films

PDDA/PSS LbL multilayer films were fabricated onto the as-prepared PDDA/P4VPPS films by using the similar procedure described above. The concentration of PSS solution used for self-assembly was 2 mg/mL in acidic aqueous solution with pH 2 and 0.5 M NaCl. Free-standing PDDA/PSS multilayer films were obtained by sequentially immersing the $(\text{PDDA}/\text{P4VPPS})_m\text{--}(\text{PDDA}/\text{PSS})_n$ films into alkali solution with pH 12 for 30 min and then in ethanol.

2.5. Characterization of multilayer films

The UV absorptions wavelength of multilayer films on quartz slides were measured in the range of 400–190 nm using UV-vis spectrometer (Cary 100BIO, Varian, USA). Clean bare quartz slide was a used as reference. The intensities of the absorption peaks at 228 nm and 258 nm were monitored because they correspond to the $\pi\text{--}\pi^*$ transition of the pyridine rings in P4VPPS [29].

The nominal thickness of each absorption layer was determined by quartz crystal microbalance (QCM, Resonance Probe GmbH, Goslar, Germany). Gold-polished AT-cut quartz crystals (Maxtek) with a fundamental frequency f_0 of 5 MHz and gold electrodes were used. The quartz crystals were first cleaned two times with a piranha solution for 5 min each time followed by rinsing with deionized water and drying with nitrogen before use. The multilayer films were fabricated on the front side of the quartz crystal. Multilayers films were prepared using the procedure similar to that described above. The QCM crystal was fixed in the bottom of a home-made holder. So when the dipping solutions were poured into the holder, only the front side of the QCM crystal was contact with the solutions. After drying, the frequency shift of the quartz crystal, Δf , were acquired at fundamental frequency (5 MHz), third (15 MHz) and fifth (25 MHz) overtones. The areal mass of the each layer, Δm , could be calculated by using Sauerbrey's equation [31]:

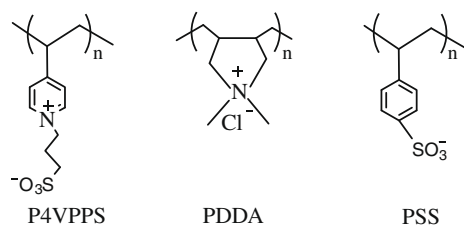


Fig. 1. Chemical structures of P4VPPS, PDDA and PSS.

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