



Full Length Article

Asymmetry of the free-standing polyelectrolyte multilayers

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ABSTRACT

Free-standing polyelectrolyte multilayers (PEMs) triggered an intense research effort to develop functional capsules and membranes, nevertheless, the comprehensive understanding of the surface distinctions between the two sides of the free-standing PEMs has been rarely studied. In this paper, we demonstrate the asymmetric surface morphologies, compositions, surface charge and wetting properties of the free-standing PEMs made of alternating deposition of poly(diallyldimethylammonium chloride) (PDDA) and poly(styrenesulfonate) (PSS) on uncharged trimethoxy (octyl) silane modified silicon wafer (TMOS-Si) substrates. The growth behaviors (e.g., linear or exponential growth) of the (PDDA/PSS)_n PEMs deposited on TMOS-Si substrates are similar to those deposited on negatively charged substrates except a slower evolution in morphology and thickness, evidenced by atomic force microscopy (AFM) and ellipsometry. The surface charge of the two sides can be tuned as +/+, -/-, and +/- by selecting the first and the terminate layer of the polyelectrolyte during the deposition process, indicated by X-ray photoelectron spectroscopy (XPS) and the surface zeta potential measured by spinning disk method. Further, water contact angle measurements exhibit a strong difference between the back side (the bottom side that was initially contacted with the substrate) ($74 \pm 4^\circ$) and front side ($33 \pm 2^\circ$ and $48 \pm 3^\circ$ for PDDA and PSS as the outmost layer, respectively) of the PEMs. The larger water contact angle of the back side is probably resulted from the orientation of the alkyl chains of the polyelectrolytes as the hydrophobic-hydrophobic interactions played significant roles in deposition of a polyelectrolyte onto an uncharged substrate. This paper may gain new insights on understanding surface properties of the PEMs.

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1. Introduction

Since its introduction in the 1990s [1–3], the layer-by-layer (LbL) assembled polyelectrolyte multilayers (PEMs) have been extensively studied due to their versatile applications [4–8] and facile construction protocols with controlled film thickness, composition, and architecture [9–11]. Free-standing PEMs films, inheriting their intrinsic properties after been detached from the substrates, make it possible to directly investigate their physical and chemical properties. In this context, broader applications were exploited using free-standing PEMs as sensors, separation and filtration membranes, electronic devices, catalysis membranes, tissue engineering scaffolds, and so on [12–17]. Specifically, it often requires asymmetric or even opposing properties between the two sides of the films

to work collaboratively. For example, free-standing films made of a humidity-responsive poly(acrylic acid) (PAA)/poly(allylamine hydrochloride) (PAH) PEMs and an underlying humidity-resistant layer, can be used as a humidity responsive actuator or a walking device [18,19], arising from the large mismatch of the interfacial stress between the two sides of the film [20]. Janus PEMs with one side hydrophilic and the other side (super)/hydrophobic [21,22], were capable for unidirectional oil/water separation [23,24]. Thus, to understand the double-side surface properties of the free-standing PEMs is desired for learning their potential applications. Nevertheless, these free-standing PEMs were generally modified by post-treatments [18–24] or in the form of capsules with one spherical surface protruding outside [3,25], studies on the two sides of the pristine free-standing PEMs were rarely reported. In this study, we focused on surface properties of both back side (the bottom side that was initially contacted with the substrate) and front side of the original free-standing PEMs.

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To date, approaches for fabricating free-standing PEMs include dissolving the underlying substrate [3,26–29], dissolving the underneath sacrificial layer [30–34], incubating in an acid or alkali solution [35,36], ion-triggered exfoliation [37], and direct peeling from the low surface energy substrate [20,21,38–44]. The former four methods require additional chemical treatment of the PEMs, which may potentially alter the properties of the PEMs or introduce residues on the PEMs surfaces. For example, Lavalle and co-workers reported that the detachment of poly(L-lysine)/hyaluronic acid PEMs from polystyrene (PS) substrate in tetrahydrofuran (THF) solvent yields specific porosity and roughness in the free-standing films [28]. Ma and co-workers found H^+ and/or Cu^{2+} can effectively exfoliate the as-prepared PAA/PAH PEMs from the substrate, but Cu^{2+} residues were also detected on the film surface [37]. In addition, upon incubation of the PAA/PAH PEMs in acid solutions, a large number of micron-sized pores appeared originated from pH-induced phase separation [45]. Excitingly, a facile method, peeling the PEMs from the low surface energy substrate using a tweezer without introducing chemicals is an effective way to obtain free-standing, contaminant-free and structure-maintained PEMs [20,21,38–44]. The elastomeric [38], mechanical [39] and thermal [42–44] properties of the free-standing PEMs, assembled on uncharged Teflon substrates, were systematically investigated. However, unlike atomic-level smooth silicon (Si) wafer and mica substrate, the Teflon substrates are much rougher, which is not accurate for studying the back side topologies and other properties of the free-standing PEMs. Recently, Schlenoff et al. fabricated free-standing poly(diallyldimethylammonium chloride) (PDDA)/poly(styrenesulfonate) (PSS) PEMs by assembling the polyelectrolytes on aluminum substrate, followed by soaking the substrate-supported PEMs in NaOH solution [29]. They confirmed that the overcompensation also occurs at the back side of the PEMs upon the addition of PDPA, which is consistent with their previous findings [46].

In the present work, the PDPA/PSS PEMs were assembled on uncharged, atomic-level smooth trimethoxy (octyl) silane (TMOS) modified silicon wafer substrates, and detached from the substrates by a smooth stream of air or using a tweezer, with minimal perturbation in the film structures and compositions. The asymmetric morphologies, compositions, surface charge and wetting properties between the two sides of the free-standing PEMs were extensively studied.

2. Experimental section

2.1. Materials

PDPA (M_w 100,000–200,000), PSS (M_w 70,000), trimethoxy (octyl) silane (TMOS, $C_{16}H_{26}O_3Si$, 96%) were purchased from Sigma-Aldrich. NaCl (99.5%), H_2O_2 (30 wt% in water) and H_2SO_4 (98%) were purchased from Chem-Supply, Australia. All the chemicals were used as received without purification. Silicon wafers were purchased from Si-Mat Silicon Materials, Germany. Quartz slides were purchased from ProSciTech. Deionized water ($> 18.2 M\Omega cm^{-1}$, Millipore Milli-Q) was used for all the experiments.

2.2. Substrate preparation

Silicon wafers and quartz slides were cleaned by immersion in piranha solution (1:3 v/v 30% H_2O_2 /98% H_2SO_4), followed by heating at 260 °C for 4 h. After cooling down to room temperature, they were rinsed with deionized water, and dried with nitrogen prior to use. The as-obtained piranha treated Si substrate will be denoted as HO-Si substrate. The uncharged hydrophobic substrates were

prepared by chemical vapour deposition (CVD) method [47–50]. Typically, the above piranha treated Si wafers or quartz slides were dried at 80 °C in an oven for 30 min before transferring into a jar. Afterwards, 30 μL of TMOS was dispensed into the jar without contacting with the substrates. Subsequently, the sealed jar was kept in an oven at 120 °C for 4 h to promote the reaction between TMOS vapor and the surface hydroxyl groups of the substrates. Finally, the jar was opened and placed in the oven at 180 °C for another 4 h to volatilize the unreacted TMOS molecules.

2.3. Assembly of the PEMs on substrates via LbL deposition

PDPA (1.0 mg/mL) and PSS (1.0 mg/mL) aqueous solutions containing 1.0 M, 0.5 M, 0.25 M and 0.1 M NaCl were prepared by dissolving PDPA and PSS into deionized water, respectively, followed by dissolving relevant amount of NaCl into the solutions under stirring prior to use. PDPA/PSS or PSS/PDPA PEMs were grown on the substrates by alternating immersion of the piranha or TMOS modified substrates into PDPA or PSS solutions with desired NaCl concentrations for 20 min, followed by thorough rinsing with deionized water. The substrates were then immersed into PSS or PDPA solutions for another 20 min and rinsed with water until the target bilayer number was obtained. Finally the substrate-supported PEMs were dried with a smooth stream of N_2 flow. The as-obtained PDPA/PSS or PSS/PDPA PEMs were designated as (PDPA/PSS) $_n$ or (PSS/PDPA) $_n$ PEMs, where “n” represents the number of bilayers. For (PDPA/PSS) $_n$ and (PSS/PDPA) $_n$ PEMs, the first deposition layer (the layer directly contacted with the substrate) is PDPA and PSS, respectively. To name a few, for (PDPA/PSS) $_{15.0}$ and (PDPA/PSS) $_{15.5}$ PEMs, the first layers are both PDPA, while the outmost layers are PSS and PDPA, respectively. For (PSS/PDPA) $_{15.0}$ and (PSS/PDPA) $_{15.5}$ PEMs, the first layers are both PSS, while the outmost layers are PDPA and PSS, respectively.

2.4. Preparation of the free-standing PEMs

The PEMs with a certain thickness deposited on the TMOS modified Si wafer (TMOS-Si) substrate can be partially detached from the edges of the substrate under a gentle perturbation of a smooth stream of air flow. Afterwards, the PEMs were gently lifted with the aid of a tweezer to prompt a complete separation of the PEMs from the underlying TMOS-Si substrate.

2.5. Characterizations

XPS analysis was performed on a Kratos Axis Ultra with a Delay Line Detector photoelectron spectrometer using a monochromatic aluminium X-ray running at 225 W with a characteristic energy of 1486.6 eV; the analysis depth was approximately 15 nm into the surface of the sample. Surface morphologies of the PEMs were measured by atomic force microscopy (AFM) (Multimode 8, Bruker) in a ScanAsyst mode using Si cantilevers. Scanning electron microscopy (SEM) images were captured on the FEI Quanta 450 operated at 10–20 kV. UV–vis absorption spectra were recorded on a UV-2600 Spectrophotometer (Shimadzu). Water contact angles (CAs) were measured on a contact angle system (Dataphysics OCA 20) according to sessile drop method, the volumes of water in all measurements were 2 μL , each of the contact angle value showed was an average of five measurements. Thickness of the PEMs was measured by an ellipsometer (J. A. Woollam Co., Inc. V-VASE) at incident radiation angle from 65° to 75° with a 5° increment using a refractive index of 1.456. Zeta potential of the PEMs was measured by spinning disk method reported by Sides and Schlenoff [51–53]. In our study, the experiments were performed on ZetaSpin Model 1.2 system using 1 inch diameter Si wafers as spinning disks; the electrolyte was NaCl with concentration of 10^{-3} M (pH 5.6) and the

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