Functional layer-by-layer multilayer films for ion recognition†

Hao Gu,ab Rongji Dai,b Yen Weiac and Hai-Feng Jia*

A layer-by-layer (LBL) nanofilm technique was introduced for surface modification in the early 1990s.1–5 The term coined by Decher6 refers to a method involving resaturation of polycation adsorption, resulting in the reversal of the terminal surface charge of the film after deposition of each layer. LbL is now employed for the fabrication of ultrathin multilayer films from charged polymers (polymions), nanoparticles (metallic, semiconducting, magnetic, ferroelectric, insulating), nanoplates, proteins, dyes, and other supramolecular species.6–11 The formation of polymeric layer-by-layer multilayer films is economical and readily amenable to scaling-up for the fabrication of large-area, defect-free devices on virtually any kind and shape of a surface.12,13 The oppositely charged species are held together by strong ionic bonds and form long-lasting uniform and stable films that are often impervious to a solvent. Forces between binder layers govern the spontaneous LbL self-assembly of ultrathin films. The forces are primarily electrostatic and covalent in nature, but they can also involve hydrogen bonding, hydrophobic, and other types of interactions.

The LbL multilayer technology has a wide variety of applications including drug delivery,14 electronic and photonic devices,15 artificial muscles,16 membranes for material separation,17 and sensors.18–23 In sensing applications, sensors that are modified with LbL multilayers offer superb sensing performance compared to those modified with monolayers or bulky polymer films: (1) a LbL multilayer film is thicker than a monolayer, so the sensing signal of a multilayer-modified sensor is stronger than those with monolayers. Meanwhile, a LbL multilayer film is typically nanometer-scale thick to ensure fast response of a sensor; (2) the thickness of LbL multilayer films can be readily controlled with high reproducibility, which cannot be readily achieved when a bulky film is prepared by means of drop-casting or spin coating methods. To date, LbL multilayer films have been successfully applied for electrodes,18–20 quartz crystal microscopy (QCM),21 spectroscopic,12,22 and micromechanical sensors.23 In these sensors, enzymes are the major sensing components in multilayer films on various sensor transducers. It is expected that a large number of chem/biosensing nanofilms can be prepared when multilayer films are doped with molecular or ionic receptors, such as crown ether, cycloextrin, or calixarene derivatives.

Although a significant number of studies have been carried out on the LbL multilayer procedure, characterization, and various applications, molecular-receptor functionalized multilayer films have not been developed, probably because receptor-containing polyelectrolytes are not readily synthesized. An alternative approach is to generate LbL multilayer films with polyelectrolytes and small molecular receptors, since a multilayer film can be prepared from polyelectrolytes with small molecules or nanoparticles. In this work, we demonstrate that this is a viable approach and we report ion-selective thin films that are built with ion-recognition agents embedded in LbL multilayer films. The ion-selective multilayer films may have wide applications in ion separation, collection, and detection.

We used three crown ethers as ion-recognition agents for proof of concept in this work. The crown ethers include 1-aza-18-crown-6 (A18C6) and benzo-18-crown-6 (B18C6) for K+ recognition,24 B15C5-An-A18C6 for recognition of Na+ under acidic conditions and K+ under basic conditions.25

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A deionized water droplet was dropped onto a surface for static measurement and a 1 mg mL\(^{-1}\) of 15-anthracenylmethyl-1,4,7,10,13-hexaphosphate, potassium hexafluorophosphate, and sodium hexafluorophosphate were purchased from Sigma-Aldrich. 16-[10-[[2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaodecin-15-yl]methyl]-9-anthracenyl]methyl]-1,4,7,10,13-pentaoxa-16-azacyclooctadecane (B15C5-An-A18C6) is synthesized according to a literature procedure. A 1 mg mL\(^{-1}\) A18C6 solution (10 mL) in a pH 5.0 HCl solution and a 1 mg mL\(^{-1}\) PSS solution (10 mL) in water at pH 5.0 were prepared. Silicon substrates covered by a layer of gold (10 mm \(\times\) 10 mm) and bare quartz plates (10 mm \(\times\) 10 mm) were used as substrates for electrochemical and contact angle measurements and UV-visible spectra, respectively. The substrates with gold surfaces were first immersed into a 1 mM sodium 2-mercaptoethanesulfonate solution in water overnight at room temperature to form a stable monolayer of negative charge on the gold surface in order to increase the adhesion of a multilayer film on the gold surface. The quartz plate was placed in a 1% ATS solution of 95 : 5 = ethanol : water for a period of 24 hours to form a stable layer of positive charge on the quartz surface. These substrates were washed with EtOH and deionized (DI) water, respectively. The substrates were then immersed into the A18C6 solution for 20 min, rinsed with water, then immersed into the PSS solution also for a duration of 20 min and again rinsed with water. This procedure was repeated 5–10 times until a desired multilayer film of A18C6/PSS was formed. The same procedure was applied to prepare a multilayer film of B15C5-An-A18C6/PSS. To prepare a multilayer film that contains electrically neutral molecules such as B18C6, a solution of 1 mg mL\(^{-1}\) B18C6 + 1 mg mL\(^{-1}\) PSS and a solution of 1 mg mL\(^{-1}\) B18C6 + 1 mg mL\(^{-1}\) PAH were used.

Contact angle experiments and UV spectra were operated by using a stepwise method, i.e. the substrates were rinsed with water and dried in air during each step before measurements. In contact angle measurements, for each measurement, a 5 \(\mu\)L deionized water droplet was dropped onto a surface for static contact angle measurements. All experiments were carried out at 20 °C. A minimum of five plates were prepared for each of the individual experiments to obtain statistical results.

At pH 5, protonated A18C6 (pKa of the conjugate acid of A18C6 is around 9.35) interacts with negatively charged PSS via electrostatic attractions. Contact angle experiments were performed to show changes in hydrophobicity of the outermost layer of a substrate on adsorption of A18C6 or PSS in each cycle (Fig. 1). The contact angle of a water droplet increased from 39.4° to 66.4° on a MES monolayer-covered surface before and after adsorption of two layers of A18C6/PSS, indicating the formation of a less hydrophilic multilayer film on the surface. The contact angles varied from 65° to 68° when the outermost layer was PSS and A18C6, respectively, in the following cycles, indicating the formation of the (A18C6/PSS)\(_n\) multilayer film.

UV spectra of a quartz plate on alternate exposure to A18C6 and PSS (Fig. 2) further suggested the formation of a multilayer film of (A18C6/PSS)\(_n\). The UV absorbance at 285 nm (\(\lambda_{\text{max}}\) of PSS) showed a linear increase on absorption of A18C6/PSS bilayers.

The ion-selective behavior of the (A18C6/PSS)\(_n\) multilayer film was validated via electrochemical experiments according to a similar method. Fig. 3 shows cyclic voltammetric (CV) curves of an electrode covered with a (A18C6/PSS)\(_n\) multilayer film before and after exposure to alkali metal ions (Li\(^+\), Na\(^+\) and K\(^+\)) in a Bu\(_4\)NPF\(_6\)-THF solution. The effects of the metal ions on the CVs of (A18C6/PSS)\(_n\) modified electrodes are summarized in Table 1. The most significant anodic shift was observed on exposure to K\(^+\), with the first cathodic potential shifted by 101 ± 13 mV and the second cathodic potential shifted by 128 ± 11 mV. The Li\(^+\) or Na\(^+\) has minimal effects on the CVs of the
The stability tests were conducted on multilayer modified redox potential shifts of a multilayer containing 0.1 M Bu4NPF6 in the absence and in the presence of 5.0 mM MPF6 (M = Li+, Na+ or K+) at a scan rate of 1 V s⁻¹.

Table 1  Shifts (mV) of redox potential of an (A18C6/PSS)n multilayer upon addition of alkali metal ions. $E_{PC}$ and $E_{PA}$ represent the shifts of the cathodic and anodic peaks, respectively

<table>
<thead>
<tr>
<th>Metal ion salt (5.0 mM)</th>
<th>$E_{PC1}$</th>
<th>$E_{PC2}$</th>
<th>$E_{PA1}$</th>
<th>$E_{PA2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiPF6</td>
<td>6 ± 3</td>
<td>9 ± 4</td>
<td>4 ± 2</td>
<td>—</td>
</tr>
<tr>
<td>NaPF6</td>
<td>5 ± 3</td>
<td>—</td>
<td>11 ± 7</td>
<td>—</td>
</tr>
<tr>
<td>KPF6</td>
<td>101 ± 13</td>
<td>128 ± 11</td>
<td>24 ± 6</td>
<td>93 ± 15</td>
</tr>
</tbody>
</table>

These results validated the K⁺-recognition characteristic of the (A18C6/PSS)n multilayer film and suggested that K⁺-induced redox potential shifts resulted from complexation of A18C6 with the K⁺. The stability tests were conducted on multilayer modified sensors with 1 month storage in air. The CVs of these electrodes showed a similar profile as those in Fig. 3.

Similarly, B18C6 and B15C5-An-A18C6 also form a multilayer film with polyelectrolytes, which was found from contact angle and UV spectra. B18C6 was embedded in a PSS/PAH multilayer film when a solution of 1 mg mL⁻¹ B18C6 + 1 mg mL⁻¹ PSS and a solution of 1 mg mL⁻¹ B18C6 + 1 mg mL⁻¹ PAH were used.

The shifts of a multilayer film of (BC18C6-PSS/BC18C6-PAH)n were not as significant as those of (A18C6/PSS)n, but also demonstrated its selectivity toward K⁺ as shown in Table 2.

We also investigated the ionic recognition characteristic of a multilayer film by means of a fluorescent method with B15C5-An-A18C6 as a model compound (Fig. 4). B15C5-An-A18C6 had been reported as a K⁺ sensor under basic conditions. It is selected to demonstrate the sensing behavior of a multilayer film under both acidic and basic conditions. As expected, the B15C5-An-A18C6-embedded multilayer film showed a Na⁺-responsive characteristic in low pH and K⁺-responsive characteristic in high pH aqueous solutions (Fig. 4). It is noteworthy that Fig. 4 demonstrates the fluorescence spectra of a (B15C5-An-A18C6/PSS)n multilayer on exposure to metal ions in aqueous solutions. The fluorescence changes of the multilayer film showed similar behaviour to metals ions in organic solvents (Fig. S1 in the ESI†).

In conclusion, we demonstrated a new class of LbL multilayer films that contain ion-recognition reagents for detection of metal ions by means of electrochemical and fluorescent methods. It is expected that these multilayer thin films will have broad applications in the field of sensing, ion transportation, collection, separation, ion-recognition induced drug release etc. It is also expected that these multilayer films can be applied on other sensing transducers, such as micromechanical, surface plasmon resonance, etc. Future work includes sensor responses to solutions containing different concentrations of metal ions for detection limit, sensing range, stability, and response time. There is an obvious advantage of the use of the multilayer films in environmental and biomedical applications due to the marvelous versatility of composition, size, and shape afforded by the LbL fabrication method. The functionalized multilayer films developed may be directly extended to other sensing devices and the approach can be generally used for recognition of anions and electrically neutral molecules by interchanging molecular receptors, such as crown-ethers, calixarene derivatives, cyclodextran, calixcrowns, etc.

Table 2  Shifts (mV) of redox potential of the (BC18C6-PSS/BC18C6-PAH)n multilayer on addition of alkali metal ions. $E_{PC}$ and $E_{PA}$ represent the shift of the cathodic and anodic peaks, respectively

<table>
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<tr>
<th>Metal ion salt (5.0 mM)</th>
<th>$E_{PC1}$</th>
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</thead>
<tbody>
<tr>
<td>LiPF6</td>
<td>5 ± 2</td>
<td>—</td>
<td>2 ± 1</td>
<td>—</td>
</tr>
<tr>
<td>NaPF6</td>
<td>11 ± 4</td>
<td>8 ± 2</td>
<td>—</td>
<td>12 ± 6</td>
</tr>
<tr>
<td>KPF6</td>
<td>22 ± 6</td>
<td>52 ± 9</td>
<td>20 ± 7</td>
<td>29 ± 8</td>
</tr>
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</table>

Acknowledgements

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Notes and references