Effects of film structure on electrochromic properties of the multilayer films containing polyoxometalates

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Multilayer films of tungstophosphate anion (P$_2$W$_{18}$) and poly(allylamine hydrochloride) (PAH) were fabricated on quartz and ITO substrates by layer-by-layer self-assembly method. These films were characterized by UV–vis spectroscopy, cyclic voltammetry (CV), chronocoulometry (CC) and atomic force microscopy (AFM). The effects of film structure on multilayer electrochromic properties were investigated. The electrochromic responses of the composite films were related to the surface coverage of anion and multilayer thickness. It was found that higher concentration of polycation and anion, or adding salt to the polycation solution used for multilayer film preparation led to thicker and denser film structure which improved optical contrast and coloration efficiency whereas prolonged response time.

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1. Introduction

Polyoxometalates (POMs) represent a well-known class of structurally well-defined metal oxide clusters with wealthy framework topologies, compositions and possess diverse properties such as catalytic activity, magnetism and luminescence [1–6]. POMs are of particular interest in electrochromic material due to their ability to act as an electron reservoir, thereby giving rise to colored valence state species while retaining their structural integrity [7–10]. Because most POMs are water soluble, they are promising candidates for the layer-by-layer (LbL) assembly technique. Over the past decade, several publications reported the successful fabrication of multilayer containing POMs and polyelectrolytes [11–13].

The LbL self-assembly method is a simple and versatile technique to prepare polymer thin film. The most important property of this method is that it affords molecular-level control over polyelectrolyte deposited from solution. Many factors such as pH, deposition time, salt concentration and solvent composition can directly influence the thickness, interfacial interactions and surface topography of the multilayer films. Among them, salt concentration has the strongest influence on the resultant film structure [14–17].

Electrochromic multilayers based on POMs and polyelectrolytes have been studied for several years, and many works have been reported [18–23]. It is noted that the conditions employed in building electrochromic Lbl films based on POMs have been modified to distinct, individual patterns. Moriguchi and Fendler reported a stable electrochromic property of self-assembled thin films by alternative deposition of sodium decatungstate and poly(diallyldimethylammonium) chloride (PDDA) [18]. In that work, the concentration of anion cluster in dipping solution was 10 mM, and no additional salt was added to the polyelectrolyte solution. The response time of coloration was 20–180 s and the bleaching time was 80–300 s, corresponding to 3–10 layers of the W$_{10}$O$_{40}^{4–}$ unit. In the latter work, the authors employed the Preyssler-type heteropolytungstate (Eu-P$_2$W$_{18}$) as an active component to assemble electrochromic multilayer films [19]. They used POMs solution at relatively lower concentration (0.5 mM) and polyelectrolyte solution containing 1 M NaCl to construct thin films. In that case, they improved the optical contrast and the response time by at least one order of magnitude compared with the former. More recently, we have been conducting detailed examination of the electrochromic performance of Dawson-type tungstophosphate and their derivatives [20–23].

In terms of general observations, although the films showed well-defined electroactivity, significant differences of the electrochromic properties were observed upon varying film structure. It is interesting that the electrochromic properties can be adjusted through controlling the film structure and assembly process. In this study we investigated the effects of film structure on the electrochromic performance of Lbl films assembled from inorganic nanoparticle tungstophosphate (P$_2$W$_{18}$) and weak polyelectrolyte poly(allylamine hydrochloride) (PAH). The PAH/P$_2$W$_{18}$ multilayer films were fabricated under conditions with three primary variables: the concentration of two components (PAH and P$_2$W$_{18}$) and NaCl added to the polycation solution, which are important factors controlling the film structure. These results show that a judicious combination of materials and film structure can lead to enhanced electrochromic properties of layer-by-layer films, in which con-
trol at the molecular level can be achieved. The understanding obtained from this study can be applied to design electrochromic Lbl films based on POMs and other functional inorganic materials.

2. Materials and methods

2.1. Materials

Tungstophosphate $K_2[\text{P}_2\text{W}_{18}\text{O}_{62}]-14\text{H}_2\text{O}$ ($\text{P}_2\text{W}_{18}$) was prepared according to literature method and identified by UV–vis adsorption spectra and cyclic voltammetry [24]. Poly(styrenesulfonate) (PSS) (MW 70,000), poly(allylamine hydrochloride) (PAH) (MW 70,000) and 3-aminopropyltrimethoxysilane were purchased from Aldrich and used without further treatment. The water used in all experiments was deionized to a resistivity of 18 MΩ cm. All polymer solution concentrations were quoted with respect to the monomer repeat unit and pH was adjusted with HCl. The ion strength of the polyelectrolyte was adjusted with NaCl.

2.2. Multilayer preparation

Quartz substrates ($15 \times 55 \text{ mm}^2$), ITO-coated glass (on one side, about $8 \times 50 \text{ mm}^2$) and silicon wafers were cleaned according to a literature procedure [20–23]. Before assembly, a $\sim$50 Å film was deposited onto a cleaned substrate by immersing the substrate (APS/PSS precursor film) alternately dipped in the PAH and $\text{P}_2\text{W}_{18}$ solutions in air with a SPI3800N Probe Station. Monotonic increment for all $\text{P}_2\text{W}_{18}$ layers, we prepared a series of self-assembly multilayer films. The pH of PAH dipping solution varied from 2 to 7 by adding aqueous HCl. The concentration of PAH solution was $1 \times 10^{-3}$ M, in the absence of salt. Tungstophosphate was dissolved in pure water at a concentration of $1 \times 10^{-3}$ M.

The formation of PAH/$\text{P}_2\text{W}_{18}$ multilayer which was assembled on a precursor (APS/PSS) film was monitored by UV–vis spectroscopy using quartz slide substrates. Monotonic increment for all PAH/$\text{P}_2\text{W}_{18}$ multilayer films was observed over the pH range 2–7. Fig. 1 shows a representative UV–vis absorption spectrum of 12-layer PAH/$\text{P}_2\text{W}_{18}$ multilayer films with inorganic component as the outermost layers. The inset displays the plots of the absorbance values at 202 and 282 nm as a function of the number of bilayers. The feature band at 202 nm is due to the benzene chromophores in PSS. As shown in Fig. 1, these films all exhibit the characteristic absorption of $\text{P}_2\text{W}_{18}$ in the UV–vis region. The former is owing to the terminal oxygen to tungsten ($\text{O}_d\rightarrow \text{W}$) charge transfer transitions, and the latter is due to the charge transfer transitions from bridge-oxygen to tungsten ($\text{O}_b\rightarrow \text{O}_c$). Furthermore, for the first layer ($n=1$), more $\text{P}_2\text{W}_{18}$ is deposited on the APS/PSS precursor film compared with those obtained for subsequent $\text{P}_2\text{W}_{18}$ depositions. This is probably due to the penetration of nanosized particles into the precursor film [11,12]. The UV–vis spectra, the surface coverage ($\Gamma$) of $\text{P}_2\text{W}_{18}$ on the PAH layer can be calculated according to the equation $\Gamma = \frac{N_A A_{\text{bilayer}}}{2n\epsilon}$, where $N_A$ is Avogadro’s constant, $A_{\text{bilayer}}$ is the absorbance at a given wavelength $\lambda$, $\epsilon$ is the molar extinction coefficient (M$^{-1}$ cm$^{-1}$), and $n$ is the number of bilayer. Fig. 2 shows the dependence of surface coverage in the tungstophosphate adsorption on the pH of PAH dipping solution. The surface coverage of an adsorbed layer of tungstophosphate decreases when the pH of PAH dipping solution increases beyond 2. The decrease in surface coverage of $\text{P}_2\text{W}_{18}$ layer relates to the decreasing surface charge density of a previously PAH-adsorbed chain with increasing pH [26]. With decreasing pH, more PAH chains become charged [29–33] and more oppositely charged inorganic particles are needed to neutralize the surface charge of PAH chains. Hence,
the pH of PAH dipping solution was adjusted to 2 in the following experiments. The other preparation parameters of the films are summarized in Table 1.

According to the absorbance value at 202 nm and the corresponding extinction coefficient (ε202 = 1.62 × 10^5 M⁻¹ cm⁻¹), an average surface coverage of P2W18 anions per layer amounts to 6.14 × 10^13 anions/cm² or 1.63 nm² per anion for sample 1. In terms of crystal structure of tungstophosphate, the surface coverage is 5.8 × 10^13 anions/cm² in the [001] plane, 3.9 × 10^13 anions/cm² in the [010] plane and 3.0 × 10^13 anions/cm² in the [100] plane. Consequently, the average surface coverage in crystalline solid amounts to 4.25 × 10^13 anions/cm² or 2.35 nm² per anion. Thus, the amount of P2W18 surface coverage in the films is 1.44 times larger than that of the crystalline material. Apparently, more than one monolayer is immobilized on the PAH layer. One explanation may be that the aggregation of P2W18 anions on PAH layer increases the surface roughness which is an important factor for the film thickness. The increase of the surface roughness leads to two principal physical effects on polymer adsorption: (1) the surface area per unit area on the reference plane increases; (2) entropy considerations result in preferential polymer adsorption on regions of low curvature [34]. The UV–vis absorption, surface coverage and monolayer equivalent values for all samples are given in Table 2. According to Table 2, it is observed that the anion surface coverage increases slightly with the concentration of PAH, whereas apparently with the concentration of P2W18 and NaCl.

### 3.2. Electrochemistry of the multilayer films

The CV of the [PAH/P2W18]1-modified ITO electrode displays four redox peaks with formal potential at E(I) = 0.125 V, E(II) = −0.040 V, E(III) = −0.436 V, and E(IV) = −0.565 V, respectively (Fig. 3a). The stepwise growth of multilayer was also monitored by cyclic voltammetry (CV). As shown in Fig. 3b, the CV curves of sample 9 reveal the alternating ionic layers deposition from n = 1 to 10, with the outermost layer of P2W18. With the increase of film thickness, the cathodic peak potentials shift slightly toward negative potential values and the anodic peak potentials shift toward positive potential values, which probably relates to uncompensated resistance [35]. For all samples, the peak currents increase with the number of bilayer, confirming the regular deposition of the PAH and P2W18. Fig. 3c shows CV curves of [PAH/P2W18]4 multilayer at different scan rates. The peak currents of both cathodic and anionic waves are all proportional to scan rate. We deduced that the redox process of the multilayer is surface-controlled. This result is consistent with the early finding of Liu [36].

As observed in other studies [37,38], compared with [PAH/P2W18]1 monolayer, multilayer films exhibit less well-defined redox peaks. The CV curve of [PAH/P2W18]1-modified ITO electrode displays well-defined four redox peaks. However, as for the [PAH/P2W18]4 multilayer, the first two cathodic waves (peaks I and II) in monolayer become merged into one cathodic peak upon cycling, when scan rate is higher than 10 mV s⁻¹. The merging and splitting phenomena are more obvious for thicker multilayer films and at high scan rate. It is possible that the structure of the multilayer films, with strong electrostatic interaction of PAH and P2W18, influences the electron transport of the redox processes [18,37]. The electroactive species which are confined in outer layers probably undergo a more difficult electron transfer process than those in inner layers. In previous multilayer systems, it is known that protons play important roles in the charge compensation during redox processes [37]. However, protons diffusion is suppressed in the compact multilayer films, which leads to such a conversion [37–41]. Taking the outermost layer for example, the five redox processes are summarized in the following equations:

\[ P_{2}W_{18}^{3+} + 2e^- = P_{2}W_{18}^{3-} \]  
\[ P_{2}W_{18}^{3-} + e^- + H^+ = H_{2}P_{2}W_{18}^{5-} \]  
\[ HP_{2}W_{18}^{5+} + e^- + H^+ = H_{2}P_{2}W_{18}^{7+} \]  
\[ H_{2}P_{2}W_{18}^{7+} + e^- + H^+ = H_{3}P_{2}W_{18}^{9+} \]  
\[ H_{3}P_{2}W_{18}^{9+} + e^- + H^+ = H_{4}P_{2}W_{18}^{11+} \]

### Table 1

<table>
<thead>
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<th>Sample</th>
<th>PAH (mM)</th>
<th>POM (mM)</th>
<th>NaCl (M)</th>
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</tr>
<tr>
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<td>1</td>
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</tr>
<tr>
<td>13</td>
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<td>1</td>
<td>0.75</td>
</tr>
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<td>14</td>
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### Table 2

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<thead>
<tr>
<th>Sample</th>
<th>Absorption (×10^13 anions/cm²)</th>
<th>Surface coverage (×10^13 anions/cm²)</th>
<th>Equivalent monolayer</th>
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<td>3</td>
<td>0.416</td>
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<td>4</td>
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<td>1.93</td>
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<td>8.62</td>
<td>2.02</td>
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<td>9</td>
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<td>8.71</td>
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<td>0.568</td>
<td>8.79</td>
<td>2.07</td>
</tr>
<tr>
<td>12</td>
<td>0.625</td>
<td>9.66</td>
<td>2.27</td>
</tr>
<tr>
<td>13</td>
<td>0.667</td>
<td>10.29</td>
<td>2.42</td>
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<tr>
<td>14</td>
<td>0.729</td>
<td>11.28</td>
<td>2.65</td>
</tr>
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</table>
3.3. Electrochromism investigation

Visually optical contrast from transparent to blue can be seen for all samples during the potential scanning between +0.4 V and −0.9 V, indicating that the films are electrochromic. As shown in Fig. 4, the spectroelectrochemistry of \([\text{PAH/P}_2\text{W}_{18}]_{40}\) films coated on ITO substrate are investigated by double-potential experiments (from +0.4 V to −0.9 V) and the visible absorbance spectroscopy. Upon electrochemical reduction, multilayer films exhibit blue color, meanwhile, a broad adsorption band with maximum at about 650 nm is observed. The color change caused by intervalence transfer from \(\text{W}^V\) to \(\text{W}^VI\) is influenced by applied potential. With decreasing potential, the coloration degree is deepened. The blue color is bleached when more positive potential is applied. Electrochromic properties include the optical contrast, coloration efficiency, switching time and stability. The optical contrast (OC) is probably the most important parameter in evaluating an electrochromic material. In this work, OC is reported as absorbance change \(\Delta A\) at maximum absorption wavelength, during the coloring/bleaching processes. The coloration efficiency (CE) has been used extensively to measure the power requirements of electrochromic materials. CE determines the amount of electronic charge which is necessary to produce the optical change \([42]\). CE is obtained by the equation \(\text{CE} = \Delta A/Q_d\) where \(Q_d\) is injected/ejected electronic charge. Switching time is often defined as the time required for 90% of maximum absorption change between redox states. Electrochromic stability is usually associated with electrochemical stability because the degradation of the active redox couple leads to the loss of optical contrast \([42]\). Representative spectroelectrochemistry spectra are shown in Fig. 5, displaying the applied potential, current, charge and absorbance at 650 nm of \([\text{PAH/P}_2\text{W}_{18}]_{40}\) multilayer. The input electronic signal is a double-potential squared wave signal alternating between −0.9 V and +0.4 V with the period of 20 s. The optical contrast, coloration efficiency and switching time for all samples are present in Table 3. We also measured the absorbance at 650 nm of all samples after 200 cycles in the electrochemical cell. The loss of optical contrast ranged from 0.7% to 5%. The result demonstrates the high stability of the electrochromic device based on tungstophosphate.

From the above experimental results, we can learn about the effects of film structure on electrochromic properties. By comparing the \(\Delta A\), CE values and switching time among different samples, it is known that film microstructure can facilely tailor the electrochromic properties of the \text{PAH/P}_2\text{W}_{18} films. In general, the film
The electrochemical measurements were conducted in HAc–NaAc (pH 4) buffer solution.

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>ΔA</th>
<th>CE (cm²/C)</th>
<th>t₁ (s)</th>
<th>t₂ (s)</th>
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<tr>
<td>1</td>
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<td>0.127</td>
<td>28.5</td>
<td>1.7</td>
<td>1.8</td>
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<td>0.137</td>
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<td>1.9</td>
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<td>37.8</td>
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</table>

According to Tables 2 and 3, it can be seen that the optical contrast and coloration efficiency increase along with the surface coverage of tungstophosphate. This result suggests that the P₂W₁₈ anions uniformly distributes on the interface of PAH on a molecular scale. In addition, the more electroactive anions are immobilized, the larger optical contrast can be obtained.

#### 3.4.1. Influence of polycation concentration

In Table 3, as for samples 1–5, the optical contrast increases from 0.112 to 0.147. The optical contrast and coloration efficiency are maximal for sample 5. These results can be explained in terms of surface coverage. At the same anion concentration, sample 5 yields the largest film adsorption. This phenomenon maybe results from the PAH chains mainly existing as loop and tail segments rather than the train segments in the microstructure of sample 5. At low polycation concentration, each PAH chain will find many binding sites. Hence, the surface comprises a number of trains, producing a rather flat conformation. Conversely, at high polycation concentration, many PAH chains interact with the interface at the same time and each can find just a few binding sites. Therefore, the surface comprises loop and tail segments, leading to deposition of much thicker layers [43]. When a coiling PAH chain is adsorbed on the substrate, more anions are needed to neutralize the oppositely charged surface. On the other hand, samples 1–5 were deposited at PAH concentration varied from 1 to 10 mM. With 10-fold increase of the PAH concentration, the surface coverage merely increased by ~9%. For high-affinity polymer prepared from high component concentration and ionic strength is thicker and denser, causing higher electrochromic optical contrast and coloration efficiency whereas slower response time.

### 3.4. Effects of film structure on OC and CE

According to Tables 2 and 3, it can be seen that the optical contrast and coloration efficiency increase along with the surface coverage of tungstophosphate. This result suggests that the P₂W₁₈ anions uniformly distributes on the interface of PAH on a molecular scale. In addition, the more electroactive anions are immobilized, the larger optical contrast can be obtained.
adsorption, a pseudoplateau in the adsorption isotherm exists [44]. Thus, one would not expect a strong dependence of anion deposition on polymer concentration, as is observed.

3.4.2. Influence of anion concentration

The surface coverage data of samples 1 and 6–9 were obtained when the PAH concentration was held constant and the P2W18 concentration was varied (listed in Table 2). With the anion concentration increasing from 1 to 10 mM, a 10-fold increase, the surface coverage increased by ~42%. Obviously, high surface coverage promotes the optical contrast and coloration efficiency (Table 3). In terms of Roland’s study, Wang et al. treated the deposition of POMs with PDDA analogous to complex formation by a spherical particle and a polyelectrolyte of the opposite sign [35,45]. They suggested that polyelectrolyte chain probably contacted with POMs cluster over a finite length and less than a half-wrap, i.e., two repeat units, without excluding any point contact configuration during the LBL fabrication [35]. Hence, at rather low anion concentration, P2W18 anions have many binding sites to adsorb on the surface of polycation and the polycation probably tends to touch the P2W18 over a finite wrap. This process results in a somewhat stratified structure. However, with the increase of anion concentration, the repulsion between charged polymer segments is screened and the polycation probably touches the anion less than a half-wrap with simultaneous aggregation of anions. The aggregation of POMs anion on polycation surface has been found by other researchers and characterized by atomic force microscopy [46,47]. At a high anion concentration, large amount of anions are immobilized by polycation chains, i.e., more than one monolayer of P2W18 is immobilized on the PAH layer. Thus, a thicker and compact multilayer structure is formed, which gives rise to high optical contrast and coloration efficiency.

3.4.3. Influence of salt concentration

As for samples 10–14, multilayer films were adsorbed on the substrate from dilute PAH solutions containing 0.1 to 1 M NaCl. Within the range of salt concentration used, regular deposition of both PAH and P2W18 was observed. As shown in Table 2, the amount of immobilized P2W18 anions grows distinctly with increasing NaCl concentration. The amount of surface coverage for sample 14 is almost two times larger than that of sample 1. This observation is in good agreement with prior studies [35,36]. In terms of Table 3, the optical contrast and coloration efficiency increase remarkably after adding salt into PAH dipping solution. Sample 14 is ca. 2.39 times the optical contrast of sample 1 (no salt case). That is to say, all anions adsorbed in the films are electrochemically accessible. Adding salt to the polycation solution strongly reduces the mutual electrostatic repulsion of the polyelectrolyte chain. Polyelectrolyte coils become denser and denser so that they are adsorbed as three-dimensional random coil rather than in a flat conformation on the interface. As a consequence, the thickness of the individual adsorbed layers increases upon salt addition [48]. Therefore, the rather small tungstophosphate anion both adsorbs at the top of the PAH surface and also disperses into the PAH matrix, which results in the increase of anion surface coverage [35,36]. Such film structure promotes electrochromic optical contrast and coloration efficiency. A model of the film structure is shown in Fig. 6.

3.5. Effects of film structure on response time

Electrochromic device can be regarded as an electrochemical cell where optical changes occur upon electrochemical reactions of two or more redox-active materials separated by an ionic conducting layer. The response time of electrochromic devices is limited by diffusion of ions from one layer to another [42]. As for the POMs-based electrochromic material, excess negative charge is injected into the multilayer during reduction with simultaneous coloration of the film. Given that the net electronic charge within a multilayer must be zero, charge compensation must be provided by anions exiting the multilayer, or by cations entering. The tungstophosphate anions within the structure are trapped in the chains of polycation and thus immobile. Hence, it is possible that cations, i.e., protons, are the major charge-compensating counterion.

At the same condition of applied potential and electrolyte solution, the response time is mainly dependent on the film thickness and morphology of the thin film. As shown in Table 3, the coloration and bleaching time of these multilayer films is in the range of 1.6–3.4 s and 1.5–3.3 s, respectively. The response time increases obviously with NaCl addition in the PAH solutions. The response time is rapid for sample 1 whose film structure is loose, owing to a rather flat conformation of PAH. The rapid response time is a direct result of extensive interpenetration within multilayer which allows a high flux of charge-compensating protons to pass between electrodes. However, by increasing anion concentration or adding salt to the polycation solution, the proton diffusion is impaired because of the compact coiling film structure, which has been described previously by electrochemical investigation.

3.6. AFM investigation

Atomic force microscopy (AFM) images demonstrate the changes in surface topology by varying the assembly conditions. Figs. 7a, 7b and 7c display AFM images of [PAH/P2W18]2 multilayer with the same preparation conditions as samples 1, 9 and 14, respectively. These [PAH/P2W18]2 multilayer are correspondingly named as samples 15, 16 and 17. Before P2W18 adsorption, the surface topography of the precursor film is uniform and smooth, consistent with previously published result [49]. After P2W18 adsorption, the mean surface roughness of the films increases and the surface comprises multitude of small domains. These domains are evidences for the aggregation of P2W18 anions. In addition, vertical grain structure of the multilayer surface can be observed from three-dimensional AFM images which show that the distribution of aggregated anions is almost uniform.

The surface height variation for sample 15 is ca. 15 nm and the surface comprises small domains with diameter of 20–30 nm (Fig. 7a). These domains (aggregated P2W18 anions) were loosely dispersed on the interface of PAH. However, the surface height variations for samples 16 and 17 are 19 and 33 nm, respectively. Moreover, the surfaces comprise packed domains with diameter about 30–50 nm (Figs. 7b and 7c). Comparing Fig. 7a with Fig. 7b, it is found that the size of the domains increases when the concentration of tungstophosphate increases from 1 to 10 mM. Similarly, the size of the domains increases when the concentration of NaCl increases from 0 to 1 M (Figs. 7a and 7c).
4. Conclusion

In this paper, a series of PAH/P$_2$W$_{18}$ films were fabricated. The influences of film structure on the electroluminescent properties of the multilayer were investigated through various fabrication conditions. Spectroelectrochemical and electrochromic characterizations of assembled films reveal that high concentration of polycation, anion and salt produces thicker and denser film structure, leading to high optical contrast and color efficiency whereas slow response times. Among the three parameters discussed above, salt concentration has the strongest influence on the electrochromic multilayer structure. By adjusting multilayer structure properly, dramatic changes of the optical contrast and response time can be realized. Our investigation will be helpful for designing efficient polyanion/polyelectrolyte hybrid electrochromic films for practical application.

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