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## Thin Solid Films

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## Counterions in polyelectrolyte multilayers: A vehicle for introducing functionalities

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## ARTICLE INFO

## Article history:

Received 21 March 2009

Received in revised form 18 June 2009

Accepted 24 June 2009

Available online 2 July 2009

## Keywords:

Multilayers  
Self-assembly  
Counterion  
Ion exchange  
Nanoparticles

## ABSTRACT

Counterions present at the surface of polyelectrolyte multilayers were utilized for the introduction of charged species into the multilayer via ion exchange. A typical polyelectrolyte multilayer film with Na<sup>+</sup> counterions in the outermost layer was immersed in an AgNO<sub>3</sub> aqueous solution and the rapid ion-exchange process was complete within 1 min. The silver ions thus introduced were then reduced *in situ* and silver nanoparticles were produced at the surface of the multilayer assembly. This example demonstrates that the counterions naturally occurring in every polyelectrolyte multilayer film can be a convenient vehicle for the introduction of various functionalities to the film.

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## 1. Introduction

Polyelectrolyte multilayers (PEMs) can be conveniently prepared via the layer-by-layer (LbL) electrostatic assembly technique. Through alternating adsorption of oppositely charged species, thin films with well-defined composition, structure, and thickness can be prepared [1–4]. This simple, versatile and inexpensive method is generally applicable to various substrates of different sizes and shapes as long as the substrate supports charge [1–4]. It is often desirable to introduce various functionalities to the PEMs, and several methods have been developed, such as grafting of polyelectrolytes by functional moieties [5], binding metal ions with a polyelectrolyte before it is assembled [6–8], using functional molecules as building blocks [9], and post-diffusion of functional molecules into the multilayers [10–13]. For multilayers assembled from weak polyelectrolytes, it has been shown that free carboxylic acid binding sites can be incorporated by controlling the pH of the polyelectrolyte dipping solutions, and then used to bind inorganic ions via ion exchange which can subsequently be converted into nanoparticles [14–18]. In this approach, the weak polyelectrolyte such as poly(acrylic acid) essentially becomes a copolymer with carboxylate and carboxylic acid units at suitable pH; while the ionized carboxylate groups are responsible for the electrostatic assembly with a polycation and end up forming ion pairs, the remaining nonionic carboxylic acid groups are then available for subsequent ion exchange for the introduction of inorganic ions. However, this methodology is only applicable to multilayers

assembled from a limited number of weak polyelectrolytes, and careful adjustment of pH is required.

On the other hand, in all PEMs there is a common structural feature that is seldom utilized. In a typical multilayer film based on either weak or strong polyelectrolytes, although the ionic groups are paired in the multilayer, at the surface of the film there are excess ionic groups with small counterions of the last deposited polyelectrolyte chains due to charge over-compensation in the deposition [19]. In the LbL assembly process, by using the same polyelectrolyte with different counterions, it has been shown that counterions can affect the adsorption kinetics [20], layer thickness [21], and mechanical properties of the film [22]. In most studies concerning LbL assemblies, however, the counterions have been neglected [22]. In a recent report we demonstrated that after the multilayers are assembled, their surface wettability can be tuned by ion exchange of the counterions for the excess ionic groups in the outermost layer [23]. In the present paper we show that the excess ionic groups existing in the outermost layer of PEMs can be utilized for introducing charged functional species into thin films via ion exchange of the counterions. Because surface excess charges are always present in any electrostatic LbL film, this facile approach can be directly applied to these multilayers without other steps. We use silver ions/nanoparticles as an example in this work.

## 2. Experimental section

## 2.1. Materials

Silver nitrate (AgNO<sub>3</sub>), sodium chloride (NaCl), and sodium borohydride (NaBH<sub>4</sub>) were of analytical grade and purchased from

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Beijing Chemical Reagents Company. Poly(styrene sulfonate) (PSS,  $M_w = 70\,000$ ), and poly(diallyldimethylammonium chloride) (PDDA, 20 wt.% in water,  $M_w = 200\,000\text{--}350\,000$ ), were purchased from Aldrich and used as received. Polished silicon wafers were purchased from Wafer Works Corporation (Shanghai). Water (18.2 M $\Omega$  cm) used for rinsing and preparing all the solutions was purified with a Millipore Simplicity 185 unit.

## 2.2. Methods

Quartz and silicon wafers were immersed in boiling piranha solution (3:1 mixture of 98% H<sub>2</sub>SO<sub>4</sub> and 30% H<sub>2</sub>O<sub>2</sub>) for 20 min and rinsed with copious amounts of water. PDPA/PSS multilayers were assembled on cleaned quartz and silicon wafers following a procedure reported previously [24]. To load silver ions the multilayer films were immersed in an AgNO<sub>3</sub> solution (0.010 mol/L) for 5 min at room temperature, and then rinsed with deionized water thoroughly and dried in a N<sub>2</sub> stream. The multilayer films with silver ions introduced were immersed in a freshly prepared aqueous solution of NaBH<sub>4</sub> (0.010 mol/L) for 10 min, rinsed with deionized water for 1 min, and then dried in a N<sub>2</sub> stream.

## 2.3. Characterization

UV–vis spectra of the multilayer films deposited on quartz slides were collected on a Shimadzu UV-2450 spectrophotometer. Contact angle analyses were carried out using the static sessile drop method on a KRUSS DSA1 (version 1.80) drop shape analyzer with water as the probe liquid. Each contact angle value reported was an average of at least five independent measurements. X-ray photoelectron spectra (XPS) were obtained on a ThermoElectron ESCALAB 250 spectrometer equipped with a monochromatic Al X-ray source (1486.6 eV). The spectra were recorded at 90° takeoff angle with 20 eV pass energy. Small pieces of a multilayer film were scraped off the quartz substrate in ethanol and transferred to a copper grid or embedded and microtomed for transmission electron microscopy (TEM) observations on a JEM-2010 microscope operating at 100.0 kV.

## 3. Results and discussion

Poly(diallyldimethylammonium chloride) (PDPA) and poly(styrene sulfonate) (PSS) are typical polyelectrolytes used in LbL studies, and thus were employed here to build the multilayers. Noting that ionic strength has a great influence on the conformation of the polyelectrolytes assembled [25], 0.75 mol/L NaCl was maintained in the polyelectrolyte solutions, and a multilayer thin film, (PDPA/PSS)<sub>3</sub>, was assembled on a cleaned silicon wafer directly without any prior treatment. The outermost layer was PSS, with Na<sup>+</sup> counterions. The multilayer film was then immersed in an aqueous solution of AgNO<sub>3</sub> (0.010 mol/L) at room temperature for several minutes, removed and rinsed thoroughly with large amounts of ultra pure water (18.2 M $\Omega$  cm), and dried with a stream of nitrogen. The film was then analyzed by XPS. Survey spectra for films before and after the treatment with the silver salt solution are compared in Fig. 1.

It has been reported that in LbL multilayers, counterions are present only in the outermost layer [19,26]. In Fig. 1, the Na peaks are observed in the survey spectrum of the as-assembled (PDPA/PSS)<sub>3</sub> film, apparently from the Na<sup>+</sup> counterions in the PSS cap layer. For the same film treated with AgNO<sub>3</sub> solution, the Na peaks completely disappear, and at the same time new Ag<sup>+</sup> peaks are clearly identified. In addition, in the N1s region (Fig. 1 inset), only one peak is present at ~402 eV, identical with that for the pristine film, due to the nitrogen in the PDPA, and no extra N1s peak of higher binding energy is observed for NO<sub>3</sub><sup>-</sup> ions could be found if absorption of AgNO<sub>3</sub> by the multilayer film had occurred. In a controlled experiment, a (PDPA/PSS)<sub>3</sub>/PDPA film, assembled under identical conditions but was terminated with

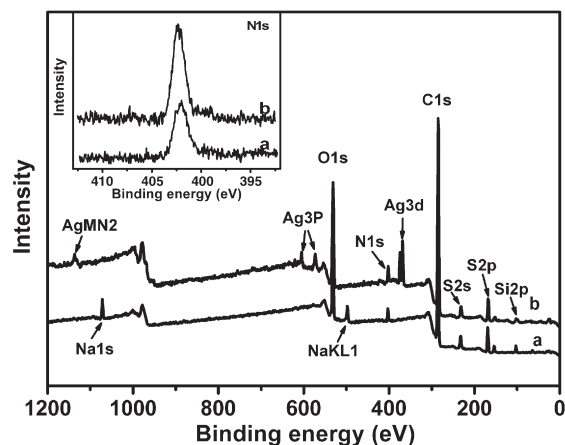


Fig. 1. XPS survey spectra of (PDPA/PSS)<sub>3</sub> multilayer film before (a) and after (b) treated with AgNO<sub>3</sub> solution (inset is the N1s region).

PDPA rather than PSS, was immersed in the AgNO<sub>3</sub> solution for an extended period of time and then examined by XPS. As Fig. 2 shows, while a weak Cl signal is present for the counterions for PDPA, no Ag signal is observed, suggesting that there was no detectable amount of adsorption/absorption of the salt to the multilayer film. These observations indicate that Ag<sup>+</sup> ions were introduced into the (PDPA/PSS)<sub>3</sub> film to replace the Na<sup>+</sup>, and that the mechanism was via ion exchange of the counterions of the multilayer and not by adsorption/absorption.

It has been found that surface wettability of polyelectrolyte multilayers with a polycation cap layer depends on the counter anion [23], and one would expect the same effect for a polyanion cap layer with different counter cations. Therefore contact angle analysis was applied here to investigate the ion exchange of the counterions, and the water contact angles for the (PDPA/PSS)<sub>3</sub> film treated with AgNO<sub>3</sub> for different times are plotted in Fig. 3. First it can be seen that the water contact angle of the multilayer surface increases by about 15° after the Na<sup>+</sup> counterion is exchanged by Ag<sup>+</sup>, probably because the R–SO<sub>3</sub><sup>-</sup>Ag<sup>+</sup> ion pair has less ionic characteristics and is less hydrated than the R–SO<sub>3</sub><sup>-</sup>Na<sup>+</sup> ion pair. In addition, the contact angle of the surface increases steeply, and reaches a plateau in less than 1 min, indicating rapid exchange kinetics, which is consistent with a surface ion-exchange mechanism. Furthermore, this quick process is advantageous over other methods to functionalize LbL films.

After Ag<sup>+</sup> ions were introduced to the surface of the multilayer film, the film was treated with NaBH<sub>4</sub> solution for 10 min to reduce the

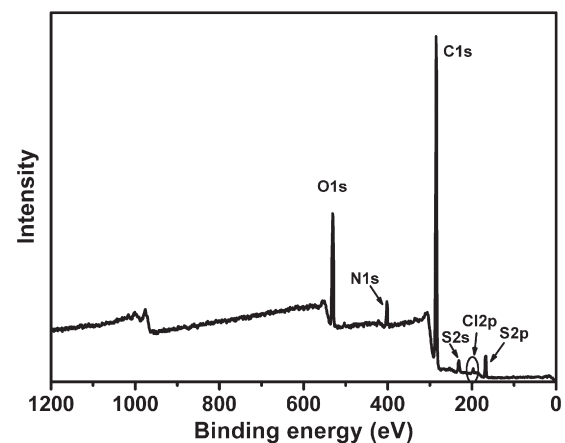


Fig. 2. XPS survey spectrum of (PDPA/PSS)<sub>3</sub>/PDPA multilayer film after treated with AgNO<sub>3</sub> solution.

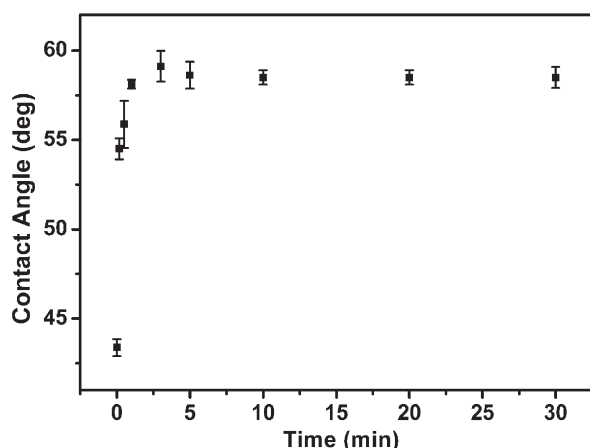


Fig. 3. Water contact angle of the surface of (PDDA/PSS)<sub>3</sub> multilayer after treated with AgNO<sub>3</sub> solution for different times.

silver ions *in situ* into silver nanoparticles [27]. Fig. 4a shows the top view of the multilayer film. Silver nanoparticles are clearly seen, and the selected-area electron diffraction (SAED) pattern in the inset

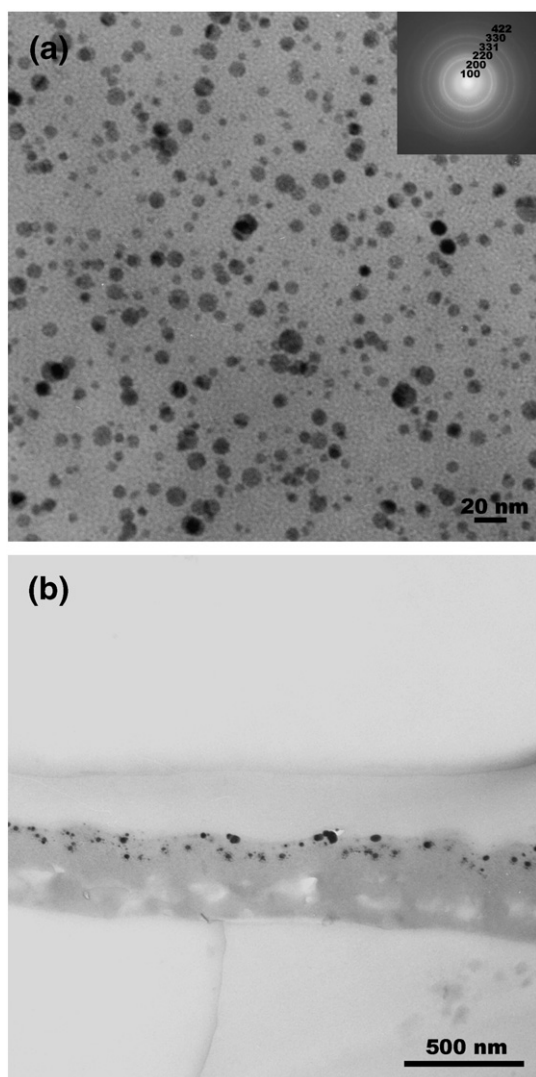


Fig. 4. TEM images of (PDDA/PSS)<sub>n</sub> multilayer films after silver ions are incorporated and then reduced to silver nanoparticles: (a)  $n=5$ , top view (inset is the SAED pattern); (b)  $n=15$ , cross section of the film.

shows the (100), (200), (220), (311), (331), and (422) diffractions of the Ag nanoparticles. Fig. 4b is a TEM image of the cross section of a (PDDA/PSS)<sub>15</sub> multilayer with Ag nanoparticles produced *in situ* after ion exchange. It can be seen that the Ag nanoparticles are confined in the top several layers. This is also a convincing evidence that counterions in electrostatic multilayers only exist at the surface, and no detectable amount of small ions are present in the bulk of the film, in agreement with the theoretical model proposed in the literature [19].

Fig. 5 displays the UV–vis spectra of the PDDA/PSS multilayers (assembled with 0.50 mol/L NaCl in the polyelectrolyte solutions) with different numbers of bilayers after Ag<sup>+</sup> counterion was incorporated and then reduced. The absorption peaks at 225 and 414 nm can be used to monitor the PSS and silver contents respectively [27,28], the intensities of which are plotted vs the number of bilayers in the inset. It is clear that the amount of PSS (and the film thickness) grows linearly after the first 2–3 assembly cycles, as reported in the literature [29]. If Ag<sup>+</sup> ions were incorporated into the bulk of the film through absorption, one would expect that the amount of silver would increase with the number of bilayers in the film [30]. The amount of silver nanoparticles observed by UV–vis remained independent of the number of bilayers in the multilayer films. This further confirms that the incorporation of Ag<sup>+</sup> ions occurs at the film surface. Fig. 6 illustrates the ion exchange and *in situ* reduction process. It should be noted that after the reduction of the Ag<sup>+</sup>, the PSS groups are again paired with Na<sup>+</sup>, which are then available for further ion exchange/reduction. Therefore, cycles of ion exchange/reduction can be applied to load multiple species or more of the same species into the same film, and this part of work will be reported elsewhere. In addition, this indicates that the approach reported here can be applied to LbL films of any number of layers.

#### 4. Conclusion

In this paper it is demonstrated that the often neglected counterions in the cap layer of an electrostatic LbL film can be utilized for introducing charged functional species into the multilayer film via ion exchange. The incorporated species are confined in the top layers of the film. Because charge over-compensation occurs in every deposition in electrostatic LbL assemblies, excess charges and counterions are always present in the outermost (polycation or polyanion) layer, and are a natural vehicle for the incorporation of charged species into multilayer films. The incorporated moieties can then be converted *in situ* to bring different functionalities, such as in the example of silver ions/nanoparticles shown here. This provides a facile and universal approach to the functionalization of electrostatic multilayer films.

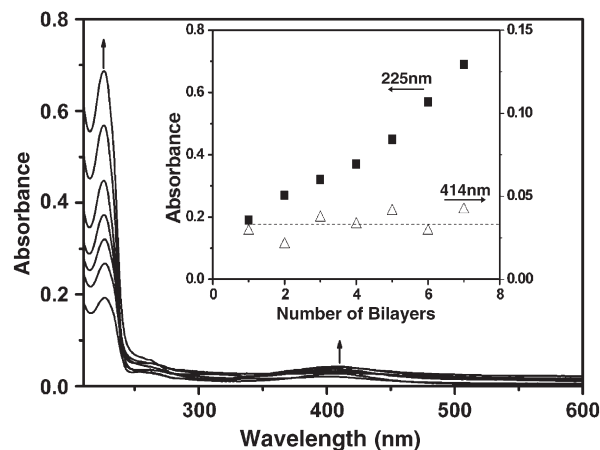


Fig. 5. UV–vis spectra of (PDDA/PSS)<sub>n</sub> multilayers ( $n=1-7$ ) after ion exchange with Ag<sup>+</sup> and *in situ* reduction by NaBH<sub>4</sub>. Inset plots the absorbances at 225 and 414 nm as functions of the number of bilayers.

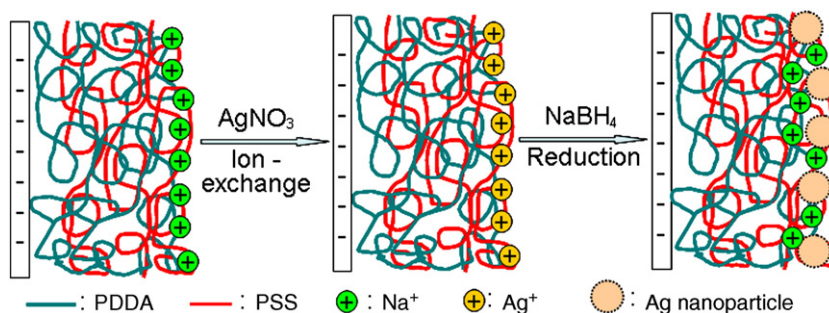


Fig. 6. Schematic illustration of the ion exchange at the surface of a multilayer film and the *in situ* reduction of the metal ions into nanoparticles.

## Acknowledgments

This work was supported by the National Natural Science Foundation of China (20423003, 20774097). Z.S. thanks the NSFC Fund for Creative Research Groups (50621302) for support.

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