Counterion exchange at the surface of polyelectrolyte multilayer film for wettability modulation†

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Counterions present at the surface of polyelectrolyte multilayers (PEMs) were utilized for modulation of surface wettability *via* ion exchange. The PEM film was dipped in aqueous solutions of different anions, respectively, and the water contact angle of the surface varied from about 10° to 120°, depending on the hydration characteristics of the anion. The ion exchange mechanism was verified by X-ray photoelectron spectroscopy. The process was rapid and reversible. Ionic strength of the polyelectrolyte solution used for preparing the PEMs was found to be crucial to the surface wetting properties and the reversibility and kinetics of the process, and the effects were correlated to the surface density of the excess charge and counterion. This work provides a general, facile and rapid approach of surface property modulation.

Introduction

Modulation of surface wettability has been a subject of intensive study because it is important for many practical applications.[1] Diverse modification procedures have been used to permanently alter the wettability of solid surfaces.[2–4] In recent years, a more challenging task in surface science has been to design smart surfaces with precisely tunable properties, where surface wettability can be changed in an accurate manner by external stimuli. The classical methods mainly concentrate on the effort of triggering the conformational or chemical changes in the films upon environmental variations, such as electrochemical potential,[5] pH,[6,7] solvent,[8] irradiation,[9,10] and ionic strength,[11–13] *etc.*

Recently, a much simpler and more versatile methodology to control surface properties has emerged, which involves tuning the wettability of a thin film on substrate by counterion exchange. It had been reported[14] that for the self-assembled monolayers on gold substrate with imidazolium ions at the tail ends, the wettability mainly depended on the nature of the counter anion, and the water contact angle changed from 23° to 65° when the Br⁻ counterion was exchanged by a bis(trifluoromethane) sulfonimide (TFSI) anion. For the imidazolium moiety terminated monolayers assembled on Si/SiO₂ substrate, the contact angle increased by 18° when Cl⁻ was replaced by PF₆⁻.[15] However, in these cases several hours were required to complete the exchange.[14,15] By using imidazolium moieties immobilized on a polyelectrolyte support assembled on ITO substrates, it was demonstrated that the same ion exchange process can be accelerated by applying a small positive potential.[16] Polyelectrolyte brushes were used to

modify surface properties and it was shown that by using completely dissimilar counterions such as polyphosphate and TFSI the contact angle of the surface can be changed reversibly by up to 75°.[17,18] These reports clearly demonstrate that the counterions in charged layers coated on solid substrates can be utilized to control the surface wettability. However, these systems reported so far require specific substrates and molecules and complex chemistry reactions for the approach to work, and thus can not be facilely applied to the modification of other surfaces.

Since its rediscovery in the early 1990s by Decher and Hong,[19] the layer-by-layer (LbL) self-assembly technique has attracted vast interest among researchers in various fields. The technique is simple, versatile, and inexpensive, and has now become a mature and effective method for fabrication of thin films as well as for modification of solid surfaces.[20] It is possible *via* the LbL approach to fabricate interfaces with a well-defined composition, structure, and thickness, thus it provides a means to control the physicochemical properties of the interfaces for applications including corrosion,[21] catalysis,[22–24] conductivity,[25] luminescence,[26] lubrication,[27,28] and adhesion.[29] The technique can be applied to modify substrates of any shape and of large sizes, as long as they support charges.[30] In the process the polyelectrolyte chains adsorbed to the oppositely-charged surface overcompensate the surface charges, resulting in so-called charge reversal of the surface so that the polyelectrolyte with opposite charges can then adsorb.[12] Generally for as-assembled polyelectrolyte multilayers (PEMs), charges on the polycation and the polyanion balance each other quantitatively with no salt ions present in the multilayer; the salt ions only reside at the surface as the counterions for the excess charges on the polyelectrolyte last deposited.[31] Although the counterions have been shown to affect the layer thickness,[32] adsorption kinetics,[33] and mechanical properties of the multilayers,[34] they were largely neglected in most studies concerning LbL assemblies.

Recently we found that the surface wettability of PEMs can be tuned using the counterions at the multilayer surface.[35] In this report, we attempt to prove the counterion exchange mechanism, and study the influence of the counterion and ionic strength on

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the surface wettability and the ion exchange kinetics and reversibility.

Experimental

Materials

Poly(diallydimethylammonium chloride) (PDDA, M_W 200 000 to 350 000), poly(sodium 4-styrene sulfonate) (PSS, M_W 70 000), perfluorooctanoic acid ($CF_3(CF_2)_6COOH$), and trifluoromethane sulfonimide (($CF_3SO_2)_2NH$) were all purchased from Sigma-Aldrich. Sodium hydroxide and all sodium salts (99.5+%) except sodium perfluorooctanate were purchased from Sinopharm Chemical Reagent Co., Ltd and used as received. Sodium perfluorooctanate (0.10 M) was prepared by reacting 0.010 mole of $CF_3(CF_2)_6COOH$ with NaOH in water and the volume of the solution was increased to 100.0 mL. Water (18.2 MΩ cm) was purified with a Millipore system and used for all the experiments.

Substrate treatment

Silicon wafers were immersed in a hot piranha solution (H_2SO_4/H_2O_2, 7 : 3 mixture) at 80 °C for 1 h and then washed with copious amount of water prior to use. Ag-coated quartz crystal microbalance (QCM) resonators were sonicated in water for several minutes and then immersed in water for about 30 min.

LbL film fabrication

PEM film was assembled by sequential dipping of a substrate in PDDA (1.0 mg/mL, with NaCl present at various concentrations) and PSS (1.0 mg/mL) aqueous solutions for 20 min each until the desired number of layers was obtained with water rinsing in between each deposition step. The counterion exchange was carried out by immersing the PEM film in an aqueous solution (0.10 M) of the sodium salt with the required anion for an appropriate time, followed by rinsing with water and drying with N_2.
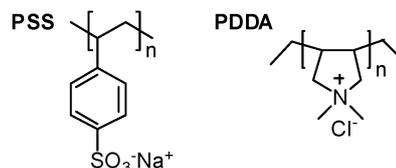
Characterization

Water contact angles were measured on a SL200D goniometer (Solon Tech. Inc., Ltd.) with standard sessile drop technique at room temperature using water (18.2 MΩ cm) as the probe fluid. A water drop was made on the needle of a syringe above the sample, and the substrate was moved up slowly until the water drop contacted the sample. Advancing contact angle was measured by subsequently adding a small amount of water to the water drop on the surface, and images of the droplet were recorded by a CCD camera. Each contact angle reported here was the average value of at least five independent measurements. X-ray photoelectron spectra (XPS) were obtained on a Thermo-Electron ESCALAB 250 spectrometer equipped with a focused monochromatic Al X-ray source (1486.6 eV). The spectra were recorded at a 90° takeoff angle (between the sample surface and the detector) with 20 eV pass energy. A homemade quartz crystal microbalance (QCM) was employed to detect the mass change of the multilayers using a 9 MHz quartz resonator coated with Ag on both sides. The QCM frequency shifts were monitored with a Protek C3100 universal frequency counter.

Results and discussion

PDDA and PSS, shown in Scheme 1, are typical strong polyelectrolytes and are often used in LbL assemblies, therefore they were used in this study to construct PEMs on silicon wafers with PDDA as the cap layer. For multilayer films, it is widely known that the wettability in most cases is determined by the outermost layer of about 5–10 Å thickness.[1,36,37] In the assembly process, while charges on the polycation and the polyanion balance each other quantitatively in the multilayer, there are excess charged groups at the surface on the polyelectrolyte last deposited (the outermost layer) with corresponding counterions. Therefore these small amounts of counterions in the outermost layer, largely neglected in most assembly studies, provide a platform for modulation of the wettability of PEMs.[35]

We set out to investigate the effects of different counter anions, including some anions in the Hofmeister series,[38] using (PDDA/PSS)$_3$/PDDA multilayers deposited on silicon wafers with 1.0 M NaCl present in the PDDA aqueous solution (denoted PE-1). The advancing water contact angles of the PE-1 with various counter anions introduced are shown in Fig. 1. It can be seen that the contact angle of the PEM can vary from approximately 10° with F^- to 120° with perfluorooctanate (PFO) as the counter anions. This magnitude of variation is comparable with that reported for substrates modified with a chemisorbed alkyl-terminated assembled monolayer.[39]

Since Hofmeister recognized the importance of ion-specific effects,[38] substantial attention has been paid to the phenomena due to the relevance to a broad range of fields. As shown in Fig. 1, the contact angles of the films bearing F^-, Cl^-, Br^-, I^-, NO_3^-, and ClO_4^- counter anions, respectively, are in the order of

**Scheme 1** Molecular structures of the polyelectrolytes used, PSS and PDDA.
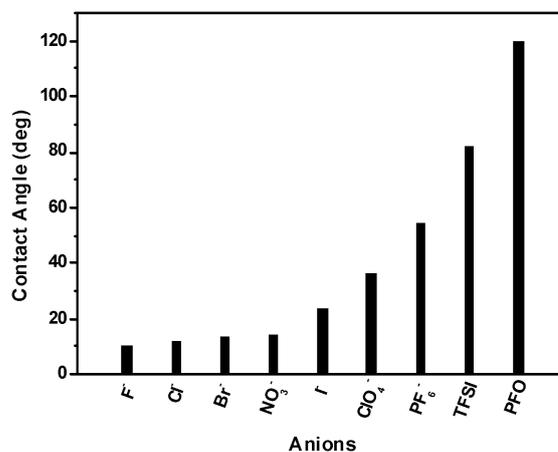
Fig. 1 Wettability of the PE-1 surfaces with different counterions.

$F^- < Cl^- < Br^- \sim NO_3^- < I^- < ClO_4^-$, which is consistent with the Hofmeister sequence in terms of the hydration characteristics of the anions. In addition, the three surfaces with counter anions bearing fluorine atoms, PF_6^-, TFSI, and PFO, respectively, are more hydrophobic, exhibiting contact angles of approximately 55°, 82° and 120°, respectively, also in the order of the hydrophobicity of the anions. Therefore the data indicate that the variation in the surface wettability of the PEMs can be attributed to the hydration capability of the counterions, in agreement with that reported previously in the literature.[14,17,35] This approach therefore can be used to quantitatively verify the hydrophobic characters of anions with great ease.

On the other hand, because of the interpenetration of the polyelectrolyte chains in the assembly, the surface of the PEM can be considered as a mixture surface, with components from the polycation and polyanion both, i.e. the surface is not completely covered by the counterions. With the presence of other polar and/or ionic groups, even when very hydrophobic counterions are introduced, it would be difficult to obtain very high contact angles, as predicted by the Cassie equation for composite surfaces.[40]

It has been previously reported that through adjusting ionic strength of the dipping solutions the thickness, surface roughness, charge density, and conformation of the PEM can be fine-tuned at the molecular level.[12,41–44] First we assembled a (PDDA/PSS)$_3$PDDA multilayer in the absence of NaCl (denoted PE-0) and compared its surface with that of PE-1 discussed above. Fig. 2 shows the contact angles of these two surfaces as-prepared and after the films were treated with a PFO solution (0.10 M). It can be seen that compared with PE-1, the surface of PE-0 is less hydrophilic than when as prepared with Cl^- counterion and less hydrophobic when the counterion is PFO, exhibiting a much smaller change of 60° vs. 108° for PE-1 in contact angle when the surface counterion is changed in between Cl^- and PFO.

The surfaces of PE-0 and PE-1 were then analyzed by X-ray photoelectron spectroscopy (XPS), and the Cl_{2p} and F_{1s} regions of the spectra are displayed in Fig. 3. For the as-assembled PE-1, a small Cl_{2p} peak (at 196.4 eV) is observed at the surface, while no fluorine is detected. After the film is treated with the PFO solution, the Cl peak disappears and a strong F_{1s} peak emerges at 689.0 eV. This is clear evidence that when PE-1 is treated with the PFO aqueous solution, the counter anion at the surface is exchanged by the PFO anion in the solution. Furthermore, Na is
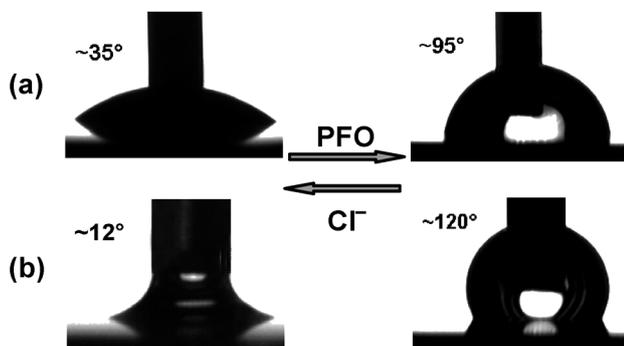
Fig. 2 Change in the surface wettability for (a) PE-0 and (b) PE-1 after the counterion is exchanged by Cl^- (left) and PFO (right).
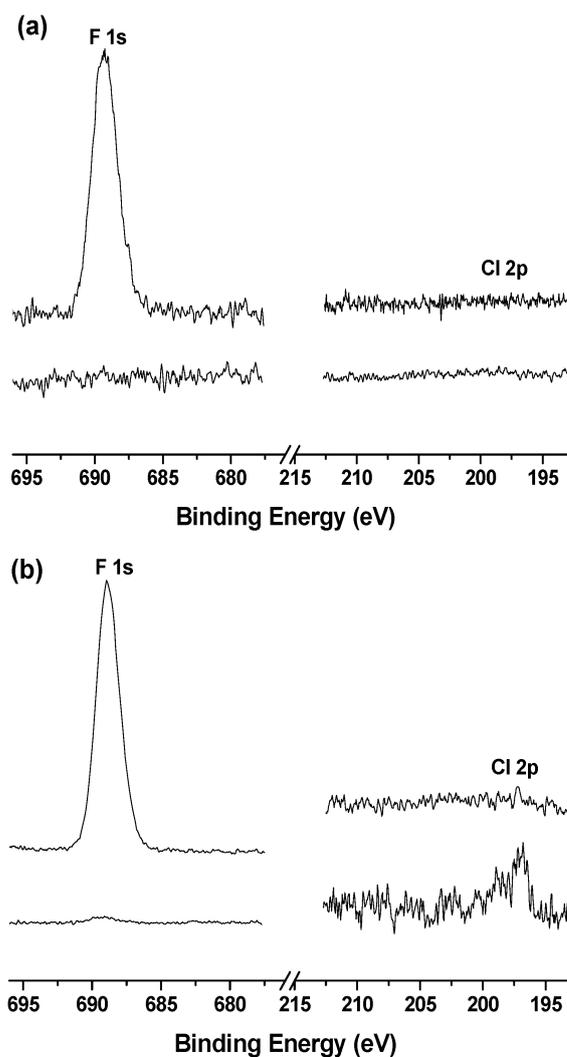
Fig. 3 The XPS spectra in the F_{1s} and Cl_{2p} regions of the surfaces of (a) PE-0 and (b) PE-1, respectively. In each panel the lower is for as-assembled PEM, and the upper is after the PEM is treated with a PFO solution (0.10 M).

not detected in either surface (spectra in the ESI†). The absence of comparable amounts of the small cation (Na^+) confirms that the PFO and the Cl^- are the counter anions for the assembled PDDA, and the contribution from salts absorbed or adsorbed, if there is any, is negligible. For the as-assembled PE-0, however, Cl is not positively identified by XPS; after the ion exchange with PFO, the F_{1s} peak is observed, with a lower intensity than that for PE-1 after exchange, which is evidenced by the much lower signal-to-noise ratio in Fig. 3(b).

As mentioned in previous sections, residual small ions within PEMs are often negligible,[31] and the excess charges and corresponding counterions exist only in the top layers. It is known that the conformation of polyelectrolyte chains is governed mainly by three factors: electrostatic interactions, solvation forces, and excluded volume effects.[45] In pure water, polyelectrolyte chains usually assume a rather stretched state because of strong electrostatic repulsion between like charges nearby and the excluded volume effects of the solvated side group. This results in low contents of excess charges and counterions, which are often not

detected by techniques such as XPS.[31] On the other hand, when salts of high concentrations are present in the solution, the charges on the polyelectrolytes are fully screened by the salt ions; the electrostatic repulsion is largely diminished, and polyelectrolyte chains would adopt an entropically more favorable coiled conformation, leading to thicker and less interpenetrating layers.[46] As a result, much more charged groups in the outermost layers are not compensated by the oppositely charged polyelectrolyte segments for lack of chance to approach them on account of being embedded in the coiled chains, leading to much higher density per area of excess charge and counterion. Therefore the PEMs assembled at high salt concentration, PE-1, have higher densities of excess charge and counterion at the surface than that of PE-0, which was assembled with no salt present, in agreement with the XPS results discussed above. When the counterion is Cl⁻, which is a hydrophilic moiety, higher content of Cl⁻ makes the surface of PE-1 more hydrophilic than that of PE-0. After the PEMs are treated with PFO solution, all the Cl⁻ counterions are exchanged with the PFO ions, ions with a big hydrophobic tail, and higher content of PFO at the surface of PE-1 results in higher hydrophobicity than that of PE-0. In addition, no Cl⁻ is detected by XPS for the as-assembled PE-0 because of its low surface content; but after the ion exchange an F_{1s} peak is observed for the (presumably same amount of) PFO ion because there are much more (15 to be exact) fluorine atoms in each PFO ion, and the XPS sensitivity factor of F is higher than Cl.[47]

Next we assembled PE-0 and PE-1 films each on a Ag-coated quartz resonator, respectively, and followed consecutive counterion exchange cycles between PFO and Cl⁻ anions by QCM. QCM is a sensitive technique that can detect mass changes occurring in a thin film by monitoring shifts in the resonance frequency of a quartz crystal on which the film is deposited. The mass change often is proportional to the (negative) frequency shift as indicated by the Sauerbrey equation.[48] Fig. 4 shows the QCM frequency shift as a function of the counterion. It can be seen that for PE-0 (Fig. 4(a)), each counterion exchange of Cl⁻ with PFO results in a frequency decrease (mass gain), and the reverse process is associated with a frequency increase (mass loss). This is in agreement with the ion exchange mechanism we have discussed, because the mass of a PFO ion (FW = 413.08) is much greater than that of a Cl⁻ (FW = 35.45). The average frequency decrease associated with the exchange of Cl⁻ by PFO was 92 ± 30 Hz, while the average frequency increase was 117 ± 20 Hz for the exchange of PFO by Cl⁻. The zigzag pattern and the rough agreement between these two numbers suggest that the exchange process is reversible. In addition, there is an overall trend of frequency increase with the increase of the exchange cycle, suggesting that the PE-0 film is not very stable in multiple treatments of salt solutions and the exchange is accompanied by desorption of the deposited polyelectrolytes.

For PE-1, the deposition of the (PDDA/PSS)₃PDDA multilayer led to a frequency decrease of 610 Hz, about 3 times that for PE-0 (data not shown), consistent with literature reports that higher ionic strength results in thicker PEMs. As shown in Fig. 4(b), PE-1 exhibits the same zigzag pattern associated with the ion exchange cycles as that for PE-0, but at a much greater magnitude and with higher consistency from cycle to cycle. The average frequency decrease for the exchange of Cl⁻ by PFO was
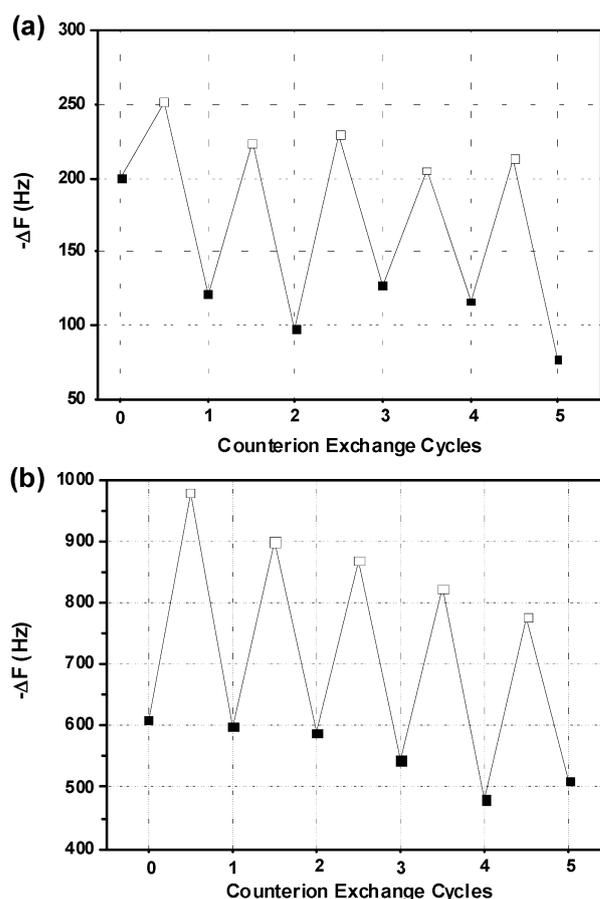

Fig. 4 QCM frequency shift ($-\Delta F$) for (a) PE-0 and (b) PE-1 upon consecutive counterion exchange between PFO (□) and Cl⁻ (■).

305 ± 37 Hz, and for the reverse process the average frequency increase was 325 ± 43 Hz. The magnitude of the frequency changes for PE-1 over the counterion exchange is about 3 times that for PE-0, indicating that many more ions are exchanged at the surface of PE-1, consistent with our contact angle and XPS results discussed above. Furthermore, it is obvious that PE-1 exhibited better reversibility and stability than PE-0 in the ion exchange process.

The results so far have shown that the ionic strength has a great effect on the excess charges at the PEM surface. To study how this then affects the surface wettability in detail, we assembled a series of (PDDA/PSS)₃PDDA multilayers at NaCl concentrations ranging from 0 to 5 M. Fig. 5 plots the water contact angle of these PEMs as-assembled (with Cl⁻ counterion) and after exchange with PFO. It can be seen that for the as-prepared PEMs, with the increase of the salt concentration, the contact angle first rapidly and then slowly decreases, and reaches a minimum value of about 12° at ∼1.0 M salt concentration. Further increase of the salt concentration leads to a slight increase of the contact angle till the NaCl is approaching saturation at 5.0 M. For the PEMs with PFO counterion, *i.e.* after the Cl⁻ counterion is exchanged with PFO, the dependence of the contact angle on the salt concentration is almost the mirror image of that for the PEMs with Cl⁻ counterion, as shown in Fig. 5. The contact angle first increases quickly and then reaches a maximum value of about 120° at ∼1.0 M salt concentration,
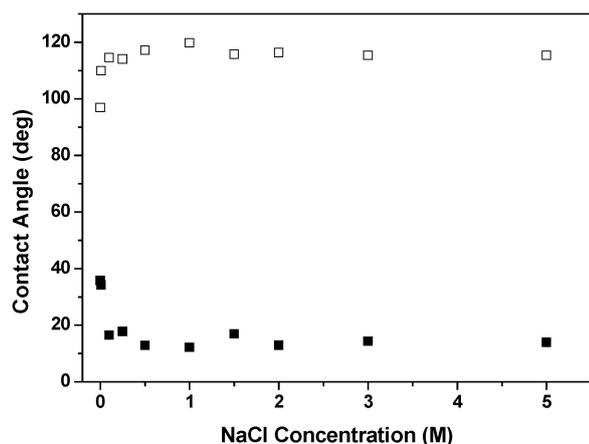
Fig. 5 Dependence of water contact angle of PEM surface bearing PFO (□) and Cl⁻ (■) counterion, respectively, on the NaCl concentration in the PDDA solution used to assemble the PEM.

Fig. 6 Contact angle as a function of counterion over consecutive exchange cycles for PEMs assembled in the presence of NaCl of 0 (■), 0.01 M (●), 0.1 M (▲), and 1.0 M (◄), respectively.

and further increasing the NaCl concentration leads to a slight decrease of the contact angle.

Zhang *et al* have used quartz crystal microbalance with dissipation (QCM-D) to investigate the influence of salt concentration on the buildup of the polyelectrolyte multilayer films, and they reported that deposition of PDDA and PSS is dominated by chain conformation at $C_{NaCl} < 1.0$ M, whereas by chain interpenetration at $C_{NaCl} > 1.0$ M, and 1.0 M is believed to be near the critical concentration for the LbL deposition from one regime to another.[43] Typically, the polyelectrolyte chains tend to change from an extended rod configuration to a globular coil conformation as the salt concentration increases. The topography of the surfaces of the PEMs we assembled at different salt concentrations were examined using AFM. The roughness distinction among these surfaces was inconspicuous (data not shown), probably because only three and a half bilayers were assembled in each film. Thus the variation in surface wettability was mainly attributed to the change in the density of the charged group at the surface, which was relevant to the conformation of the polyelectrolyte chains, and probably at $C_{NaCl} \sim 1.0$ M the charged group density at the surface was the highest as the chains adopt the most compact state.

Next we investigated the effect of the salt concentration on the reversibility of the ion exchange. Fig. 6 shows that the wettability of the PEMs assembled at various NaCl concentrations can be changed reversibly by consecutive counterion exchange between Cl⁻ and PFO. It can be seen that for the PEMs assembled at 0.1 M NaCl concentration or higher, the surfaces can be switched between hydrophilic and hydrophobic for at least 5 exchange cycles with almost complete reversibility. However, the contact angle variation decreases slightly as consecutive counterion exchange progresses at 0.01 M salt concentration, and the reversibility is much worse at salt free, probably due to the lower stability of the PEMs assembled at low salt concentrations, as we discussed above.

Finally we studied by water contact angle analysis the kinetics of the counterion exchange between PFO and Cl⁻ at the surfaces of PEMs assembled at different NaCl concentrations, respectively, and the dependence of the contact angle as a function of time the PEM is in contact with the exchanging solution is shown
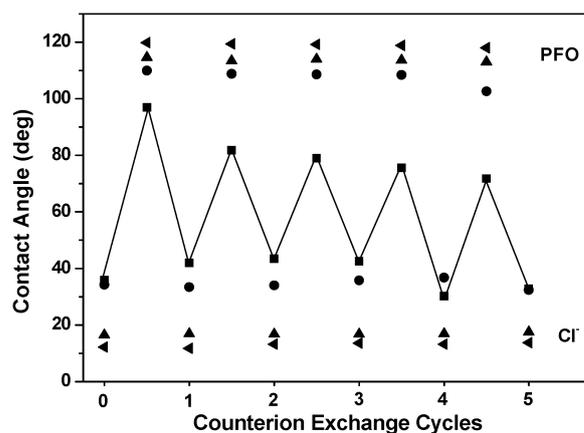
in Fig. 7. It can be seen from Fig. 7(a) that at all NaCl concentrations, the exchange of Cl⁻ by PFO is extremely fast, going to completion within 3 s. On the other hand, Fig. 7(b) shows that the time needed for Cl⁻ to replace the PFO counterion at the PEM surface is largely dependent on the ionic strength of the
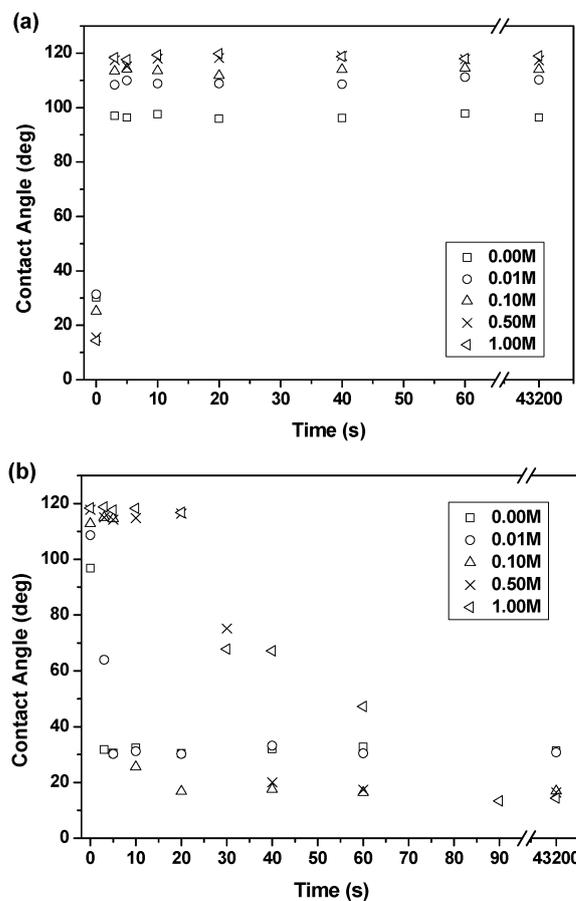
Fig. 7 Kinetics of counterion exchange at the surfaces of PEMs assembled at NaCl concentration of 0, 0.01, 0.1, 0.5, and 1.0 M, respectively: (a) Cl⁻ exchanged by PFO and (b) PFO exchanged by Cl⁻.

polyelectrolyte solution used for the assembly of the PEM. With no NaCl present, the contact angle of the PEM surface decreases immediately and reaches a plateau in 3 s, and at 0.01 M NaCl concentration, the exchange process is slightly slower and takes 5 s to reach the steady contact angle value. However, the exchange kinetics for the PEMs assembled at 0.1, 0.5, and 1.0 M NaCl concentrations appear different. In these three cases the contact angles remain high and stable after the PEM surfaces are in contact with the exchanging solution (0.10 M NaCl) for a few seconds, and then they decrease to a plateau value of below 20°. The higher the salt concentration, the longer the period the PEM retains its hydrophobicity, and the longer transition is from hydrophobic to hydrophilic plateau values. At 0.10 M NaCl concentration, 10 s are needed to turn the surface hydrophilic, at 0.50 M, the surfaces remain very hydrophobic for at least 20 s, and the transition is complete in the next 20 s, and at 1.0 M, the time for Cl^- to completely replacing PFO anions is about 90 s.

It's obvious that the exchange kinetics is a function of the surface hydrophobicity. It appears that the counterion exchange process involves two distinct steps: first the solution wets the PEM surface, during which the surface contact angle remains stable, and then the counterion exchange proceeds, where the contact angle changes. For the exchange of Cl^- by PFO, because the starting PEM surface is hydrophilic with a contact angle of <20°, the wetting of the PEM surface by the PFO solution is spontaneous and instantaneous, so we were not able to detect this step and only the exchange step was observed in our study. For the exchange of PFO by Cl^-, the time for the solution to wet the PEM surface increases with the hydrophobicity of the surface. The higher the salt concentration in the polyelectrolyte solution, the higher the PFO content at the PEM surface, and the more hydrophobic the surface is. In addition, the perfluoro tails of the PFOs may form clusters at the surface due to strong van der Waals interactions between long perfluoroalkyl chains,[49] and the segregation should be more severe at higher PFO density at the PEM surface. Therefore it takes longer for the solution to wet the surface of the PEMs assembled at higher salt concentrations as we observed. Then the ion exchange of the PFO ions bound to the PEM surface by the Cl^- ions in the solution proceeds, and the contact angle of the surface decreases to reach the plateau. This step is also a function of the ionic strength in the assembling solution since the latter affects the conformation and interpenetration of the polyelectrolyte chains deposited and the amount and distribution of the excess charges (counterions) in the outermost layer.

Conclusions

In this work we have studied in detail the modulation of surface wettability of polyelectrolyte multilayer (PEM) films by counterion exchange at the film surface. The wetting properties of the PEMs can be adjusted rapidly in a broad range from hydrophilic to hydrophobic by exchange of the counterion with anions of appropriate hydration characteristics, and the exchange mechanism has been confirmed by XPS and QCM. The advancing water contact angle of the PEM surface can vary from as low as about 10° to as high as about 120° by simply dipping the film in a salt solution for a few seconds, and the process is reversible. The ionic strength of the polyelectrolyte solution used for the

PEM assembly is crucial to the wetting properties and the reversibility and kinetics of the counterion exchange. PEMs assembled at higher salt concentrations (up to 1.0 M NaCl) not only are more stable, but also have more excess charges and correspondingly more counterions at the surface, so that they exhibit greater variation and much better reversibility in wettability over the counterion exchange. The counterion exchange involves two steps, wetting of the surface by the exchanging solution and ion exchange between the solution and the surface. The kinetics, mainly of the wetting step, is a function of the charge density of the PEM surface and therefore depends on the ionic strength of the polyelectrolyte solution. These results have demonstrated that the excess charge/counterion naturally occurring at the surface of every PEM film can be utilized to facilely tune the surface wettability. Since the LbL technique for building PEMs is simple and versatile, and more importantly is generally applicable to a large variety of substrates, the approach reported in this work could potentially be used to modulate surface properties of materials in many different fields, such as in the design of microfluidics, microengineering of smart templates and biomedical devices based on LbL technology.

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