Tunable wettability by counterion exchange at the surface of electrostatic self-assembled multilayers†

Liming Wang,[ab] Yuan Lin,[a] Bo Peng[ab] and Zhaohui Su*[a]

Received (in Cambridge, UK) 5th August 2008, Accepted 17th September 2008
First published as an Advance Article on the web 9th October 2008
DOI: 10.1039/b813557f

A novel method to tune surface wettability rapidly and reversibly has been developed by ion exchange of the counterions at the surface of a multilayer film assembled *via* electrostatic interaction.

The design and fabrication of smart surfaces with dynamically controllable properties has become a challenging task in materials science.[1] Wettability is one of the important surface properties because it is crucial in many practical applications, such as adhesion, coating, microfluidics and superhydrophobic surfaces.[2] Surface wettability can be changed in an accurate manner by external stimuli, and the classical method is mainly concentrated on triggering the conformational or chemical changes on solid surfaces upon environmental variations, such as electrochemical potential,[3] pH,[4,5] solvent,[6] irradiation[7] or ionic strength.[5,8] A potentially more versatile route to modulation of surface properties has emerged recently, which showed that the wettability of charged thin films can be tuned by choosing the proper counterions.[9] Choi and co-workers[10] reported that the wettability of monolayers self-assembled on gold substrate with imidazolium ions at the tail ends depended on the nature of the counterion, where the water contact angle increased from 25° to 65° when the Br^- counterion was replaced with bis(trifluoromethane) sulfonimide anion (TFSI). They also assembled imidazolium ion-terminated monolayers on silicon surface,[11] and observed a 18° change in contact angle when the Cl^- counterion was exchanged with PF_6^-. Several hours were needed for the exchange to complete.[10,11] Niu *et al.*[12] showed that the same counterion exchange between the surface and solution can be accelerated by applying a small positive potential using a polyelectrolyte-functionalized ionic liquid assembled on ITO. Huck and co-workers[9,13] demonstrated that the wettability of cationic polyelectrolyte brushes grafted on substrates can be changed by up to 75° using completely dissimilar counterions such as TFSI and polyphosphate. These results clearly demonstrate the tunability of surface wettability based on counterion exchange. However, the systems reported involved specific substrate chemistry for the approach to work.

The layer-by-layer (LbL) electrostatic assembly technique has now become a relatively mature and effective method for fabrication of thin films, where by alternating adsorption of oppositely charged species, thin films with well-defined composition, structure, and thickness can be obtained.[14] This simple, versatile and inexpensive method is generally applicable to a variety of substrates of different shapes and sizes as long as the substrate supports charge.[14] In the LbL assembly process, counterions have been found to affect the adsorption kinetics,[15] layer thickness,[16] and stiffness of the film,[17] but in most studies concerning LbL assemblies the counterions were neglected.[17]

In this communication we take advantage of the counterions on the surface of the LbL assemblies, and apply the well-established ion exchange chemistry to multilayers assembled by LbL technique using common polyelectrolytes on silicon substrate for the modulation of surface wettability. This simple approach involves no chemical modification of the substrate or the polyelectrolytes used, and is expected to be applicable to any substrate conferred by the LbL assembly technique.

Poly(diallyldimethylammonium chloride) (PDDA) 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 polyelectrolyte,[8] 0.25 M NaCl was maintained in the 1.0 mg mL^{-1} PDDA aqueous solution, and a multilayer thin film, $(PDDA/PSS)_3PDDA$, was assembled on a cleaned silicon wafer directly without any prior treatment following the procedure reported in the literature.[18] Advancing contact angles using ultra-pure water (18.2 MΩ cm) as the probe fluid were measured as a quantitative indication of the surface wettability. Five replicate measurements were taken for each sample, and the average and standard deviation are reported. The contact angle for the multilayer surface with Cl^- as the counterion for PDDA was ~19°, indicating a hydrophilic surface. In order to assess the stability of the wetting behavior of the surface, the contact angle was measured on a same piece of the multilayer film after it was allowed to stand in ambient for various of time, and the numbers remained the same (data in the ESI†), indicating that the surface was stable and not altered by the probe fluid, and the advancing water contact angle was a valid representation of the surface wettability. Replicates of the $(PDDA/PSS)_3PDDA$ multilayer were then immersed in a set of aqueous solutions (0.10 M) of different salts respectively at room temperature for several minutes, removed and rinsed thoroughly with large amount of

---

[a] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, China. E-mail: zhsu@ciac.jl.cn; Fax: +86 (0)431 8526 2126; Tel: +86 (0)431 8526 2854
[b] Graduate School of Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing, 100039, China

† Electronic supplementary information (ESI) available: Contact angles for the multilayer surfaces before and after ion exchange measured at various drying times. See DOI: 10.1039/b813557f

ultra pure water (18.2 MΩ cm), and dried with a stream of nitrogen. The corresponding contact angles for the multilayers after this treatment with salt solution are presented in Fig. 1.

It can be seen that the water contact angle of the LbL multilayer strongly depends on the type of the anion in the solution used to treat the multilayer. Especially the surface treated with pentadecafluorooctanate anion ($C_7F_{15}CO_2^-$) exhibits a contact angle of $114 \pm 2°$, a drastic increase from the $19 \pm 2°$ before the treatment, making the surface very hydrophobic. The contact angle remained the same (114°) for the same multilayer film after it stayed in ambient for various of time (data in the ESI†), confirming the stability of the wetting behavior of the surface. It has been previously reported that the surface wetting properties of sequentially adsorbed polyelectrolyte layers are primarily controlled by the outermost layer.[19] It is also well known that the counterions only exist at the surface of the multilayers.[20] Thus the variation in the surface wettability of the multilayer observed here is due to the exchange of the Cl^- counterions attached to the quaternary ammonium groups (QA^+) on the PDDA in the outermost layer by the various anions in the solutions. In addition, the order of the surface hydrophobicity of the multilayers with different counterions we observed was $C_7F_{15}CO_2^- > TFSI > C_3F_7CO_2^- > PF_6^- > ClO_4^- > BF_4^- > Cl^-$, which is in good agreement with that found for imidazolium ion-terminated monolayers[10] and polyelectrolyte brushes,[9] which may be attributed to the hydration characteristics of the anions.[9,10] It is conceivable that the broad wettability range we have explored, a dynamic range of 95°, may be further extended by using anions more hydrophobic than $C_7F_{15}CO_2^-$, such as perfluorodecanoate, and anions more hydrophilic than Cl^-, such as polyphosphates. Furthermore, the exchange kinetics was studied. $(PDDA/PSS)_3PDDA$ multilayers with Cl^- and pentadecafluorooctanate as the counterions for the outermost layers were immersed in aqueous solutions (0.10 M) of $C_7F_{15}CO_2Na$ and NaCl respectively for various periods of time, and rinsed and dried, and the contact angles for these surfaces are shown in Fig. 2. It can be seen that complete switch of the surface properties can be achieved within one minute, indicating fast exchange kinetics.

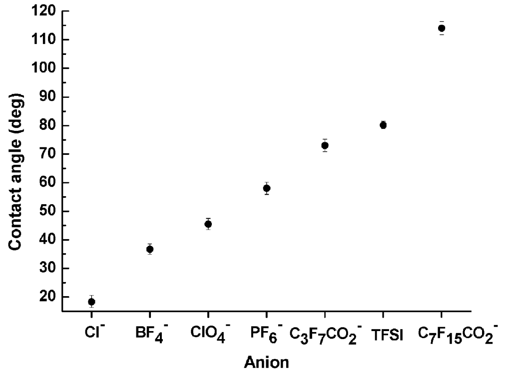

Fig. 1 Wettability of the LbL multilayers with different counterions.

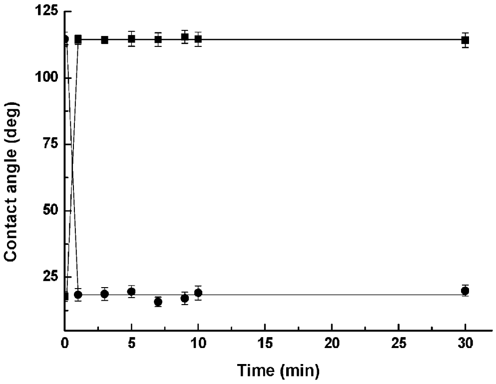

Fig. 2 Counterion exchange kinetics assessed by water contact angle for a $(PDDA/PSS)_3PDDA$ multilayer with Cl^- counterion dipped in a 0.10 M $C_7F_{15}CO_2Na$ solution (■), and a $(PDDA/PSS)_3PDDA$ multilayer with $C_7F_{15}CO_2^-$ counterion dipped in a 0.10 M NaCl solution (●), respectively.

Having established the counterion exchange for the LbL multilayers, we investigated the reversibility of the process. The multilayer on the Si wafer was alternately immersed in aqueous solutions of NaCl and $C_7F_{15}CO_2Na$ for 10 min with thorough rinse and nitrogen purge in between, and the water contact angle changed from ~20° for Cl^- to ~110° for $C_7F_{15}CO_2^-$ as the counterion for the multilayer, and moved in cycles. As can be seen in Fig. 3, within the 5 cycles we have tested, after each exchange with $C_7F_{15}CO_2^-$, the contact angle jumps to the same level of $113 \pm 2°$, and it moves back to the same $19 \pm 2°$ after an exchange with Cl^-, indicating that the change of the wetting properties is completely reversible *via* consecutive counterion exchanges between the two anions.

In summary, we have demonstrated that the surface wettability of LbL films composed of polyelectrolytes can be facilely tuned by exchange of the often neglected counterions of the outermost polycation layer. The broad wettability range attainable, rapid exchange kinetics, and complete reversibility afforded by this extremely simple approach, combined with the simplicity, versatility, and general applicability of the LbL

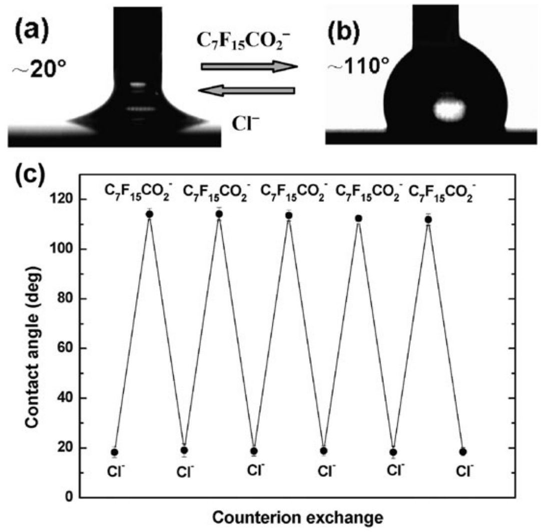

Fig. 3 Switch of the wetting characteristics of the LbL multilayer *via* the exchange of counterions between Cl^- (a) and $C_7F_{15}CO_2^-$ (b). (c) The plot of the water contact angle as a function of the counterions, showing the reversible behavior of the LbL multilayer over repeated cycles of Cl^- and $C_7F_{15}CO_2^-$ counterion exchange.

technique make it a very promising and practical route to the design and fabrication of smart surfaces with dynamically controllable properties.

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.

Notes and references

1 J. W. Feast, H. S. Munro and R. W. Richards, *Polymer Surfaces and Interfaces II*, Wiley, New York, 1993.
2 T. L. Sun, L. Feng, X. F. Gao and L. Jiang, *Acc. Chem. Res.*, 2005, **38**, 644; J. De Coninck, M. J. de Ruijter and M. Voue, *Curr. Opin. Colloid Interface Sci.*, 2001, **6**, 49; X. M. Li, D. Reinhoudt and M. Crego-Calama, *Chem. Soc. Rev.*, 2007, **36**, 1350.
3 J. Lahann, S. Mitragotri, T. N. Tran, H. Kaido, J. Sundaram, I. S. Choi, S. Hoffer, G. A. Somorjai and R. Langer, *Science*, 2003, **299**, 371.
4 J. R. Matthews, D. Tuncel, R. M. J. Jacobs, C. D. Bain and H. L. Anderson, *J. Am. Chem. Soc.*, 2003, **125**, 6428.
5 D. Yoo, S. S. Shiratori and M. F. Rubner, *Macromolecules*, 1998, **31**, 4309.
6 L. Ionov, S. Minko, M. Stamm, J. F. Gohy, R. Jerome and A. Scholl, *J. Am. Chem. Soc.*, 2003, **125**, 8302.
7 B. C. Bunker, B. I. Kim, J. E. Houston, R. Rosario, A. A. Garcia, M. Hayes, D. Gust and S. T. Picraux, *Nano Lett.*, 2003, **3**, 1723; S. Abbott, J. Ralston, G. Reynolds and R. Hayes, *Langmuir*, 1999, **15**, 8923.
8 G. Decher and J. Schmitt, *Prog. Colloid Polym. Sci.*, 1992, **89**, 160.
9 O. Azzaroni, A. A. Brown and W. T. S. Huck, *Adv. Mater.*, 2007, **19**, 151.
10 B. S. Lee, Y. S. Chi, J. K. Lee, I. S. Choi, C. E. Song, S. K. Namgoong and S. G. Lee, *J. Am. Chem. Soc.*, 2004, **126**, 480.
11 Y. S. Chi, J. K. Lee, S. Lee and I. S. Choi, *Langmuir*, 2004, **20**, 3024.
12 Y. F. Shen, Y. J. Zhang, Q. X. Zhang, L. Niu, T. Y. You and A. Ivaska, *Chem. Commun.*, 2005, 4193.
13 S. Moya, O. Azzaroni, T. Farhan, V. L. Osborne and W. T. S. Huck, *Angew. Chem., Int. Ed.*, 2005, **44**, 4578.
14 G. Decher, in *Multilayer Thin Films*, ed. G. Decher and J. B. Schlenoff, Wiley-VCH, Weinheim, 2003, p. 1; X. Zhang, H. Chen and H. Zhang, *Chem. Commun.*, 2007, 1395; J. F. Quinn, A. P. R. Johnston, G. K. Such, A. N. Zelikin and F. Caruso, *Chem. Soc. Rev.*, 2007, **36**, 707; P. T. Hammond, *Adv. Mater.*, 2004, **16**, 1271.
15 O. Mermut and C. J. Barrett, *J. Phys. Chem. B*, 2003, **107**, 2525.
16 M. Salomäki, P. Tervasmäki, S. Areva and J. Kankare, *Langmuir*, 2004, **20**, 3679.
17 M. Salomäki, T. Laiho and J. Kankare, *Macromolecules*, 2004, **37**, 9585.
18 G. Wu and Z. Su, *Chem. Mater.*, 2006, **18**, 3726.
19 W. Chen and T. J. McCarthy, *Macromolecules*, 1997, **30**, 78; D. Yoo, S. S. Shiratori and M. F. Rubner, *Macromolecules*, 1998, **31**, 4309.
20 J. B. Schlenoff, in *Multilayer Thin Films*, ed. G. Decher and J. B. Schlenoff, Wiley-VCH, Weinheim, 2003, p. 99, and references therein.