

# Ion-Specific Oil Repellency of Polyelectrolyte Multilayers in Water: Molecular Insights into the Hydrophilicity of Charged Surfaces\*\*

Xiaokong Liu, Chuan Leng, Li Yu, Ke He, Lauren Joan Brown, Zhan Chen, Jinhan Cho, and Dayang Wang\*

**Abstract:** Surface wetting on polyelectrolyte multilayers (PEMs), prepared by alternating deposition of polydiallyldimethylammonium chloride (PDDA) and poly(styrene sulfonate) (PSS), was investigated mainly in water-solid-oil systems. The surface-wetting behavior of as-prepared PEMs was well correlated to the molecular structures of the uncompensated ionic groups on the PEMs as revealed by sum frequency generation vibrational and X-ray photoelectron spectroscopies. The orientation change of the benzenesulfonate groups on the PSS-capped surfaces causes poor water wetting in oil or air and negligible oil wetting in water, while the orientation change of the quaternized pyrrolidine rings on the PDDA-capped surfaces hardly affects their wetting behavior. The underwater oil repellency of PSS-capped PEMs was successfully harnessed to manufacture highly efficient filters for oil-water separation at high flux.

A study of water wetting on a charged surface will not only advance our knowledge of many peculiar surface functions, such as lubrication, anti-fouling, and self-cleaning, which are encountered in biological systems, but also enhance our ability to translate these surface functions into innovative technical applications.<sup>[1]</sup> In general, charged surfaces are easily wetted by water, which is a macroscopic expression of strong hydration of the surface ionic groups. For a solid surface, air drying is obviously inevitable in practice, even if is not required technically. Upon contact with air, charged surfaces, like many other polar surfaces with high surface free energy, must orient the ionic groups inwards to lower the surface free energy, thus resulting in a noticeable increase in surface hydrophobicity. As such, wetting charged surfaces with water, characterized by the water contact angle in air ( $\theta_{w/a}$ ), has little dependence on the surface ionic group, though the interaction of ions or ionic groups with water (hydration)

is known to be ion-specific.<sup>[2]</sup> In contrast, the present work demonstrates a prominent dependence of the surface hydrophilicity of polyelectrolyte multilayers (PEMs) on the molecular nature of the uncompensated ionic groups presented at the surface.

Herein we study surface wetting of the PEMs, which are obtained by layer-by-layer (LbL) deposition of polydiallyldimethylammonium chloride (PDDA) and poly(styrene sulfonate) (PSS), mainly in water-solid-oil systems. Our results demonstrate that the surface hydrophilicity of the resulting PEMs is correlated primarily to the molecular configuration rather than hydration strength of the uncompensated ionic groups on the surfaces. According to a newly developed theory on the correlation between the water contact angle and surface polarity,<sup>[3]</sup> the surface hydrophilicity of PEMs should be determined by the surface charge density, which can be defined by the surface area occupied by the surface ionic groups. For PSS-capped surfaces, the uncompensated benzenesulfonate ( $BS^-$ ) groups on the surfaces comprise rigid and hydrophobic phenyl (Ph) moieties and hydrophilic, anionic sulfonate ( $SO_3^-$ ) moieties, which are well separated in space (see Scheme S1 in the Supporting Information). Our spectroscopic results show that in water, the surface  $BS^-$  groups orient their Ph moieties in an orderly and upright position out of the surface of the plane. This orientation maximizes surface charge density and transforms the surface hydration of the  $SO_3^-$  moieties into oil repellency with an oil contact angle in water ( $\theta_{o/w}$ ) of greater than  $165^\circ$ . Upon contact with air or oil, the Ph moieties are randomly distributed and orient parallel to the surface plane, and thus significantly reduces the surface charge density. As a result, the PSS-capped surfaces become poorly wetted by water, as evidenced by the water contact angle in oil ( $\theta_{w/o}$ ) of greater than  $90^\circ$ . In contrast, the uncompensated quaternary amine ( $QA^+$ ) groups on PDDA-capped surfaces have their cationic ( $N^+$ ) center enveloped by four alkyl moieties in each pyrrolidine ring (see Scheme S1). Owing to this configuration, the surface charge density and surface hydrophilicity of the PDDA capped surfaces are insensitive to the orientation of the quaternized pyrrolidine ring. They remain well wetted by water in air and in oil ( $\theta_{w/o} = 42^\circ$ ), though the weak hydration of the surface  $QA^+$  groups cannot effectively prevent oil adhesion in water ( $\theta_{o/w} = ca. 133^\circ$ ). Thus, our results demonstrate a pronounced dependence of the wetting behavior of charged surfaces on the molecular nature and geometric configuration of the surface ionic groups. This dependence will also provide a better model to describe how ionic species interact with water, air, and oil at interfaces where a marked conformational change is essential for adsorption and translocation.

[\*] Dr. X. Liu, L. Yu, K. He, L. J. Brown, Prof. Dr. D. Wang  
 Ian Wark Research Institute, University of South Australia  
 Mawson Lakes, SA 5095 (Australia)  
 E-mail: dayang.wang@unisa.edu.au

C. Leng, Prof. Dr. Z. Chen  
 Department of Chemistry, University of Michigan  
 Ann Arbor, MI 48109 (USA)

Prof. Dr. J. Cho  
 Department of Chemical and Biological Engineering, Korea University, Seoul, 136-701 (Korea)

[\*\*] Australian Research Council (DP120102959) and US Office of Naval Research (N00014-12-1-0452) are acknowledged for financial support.



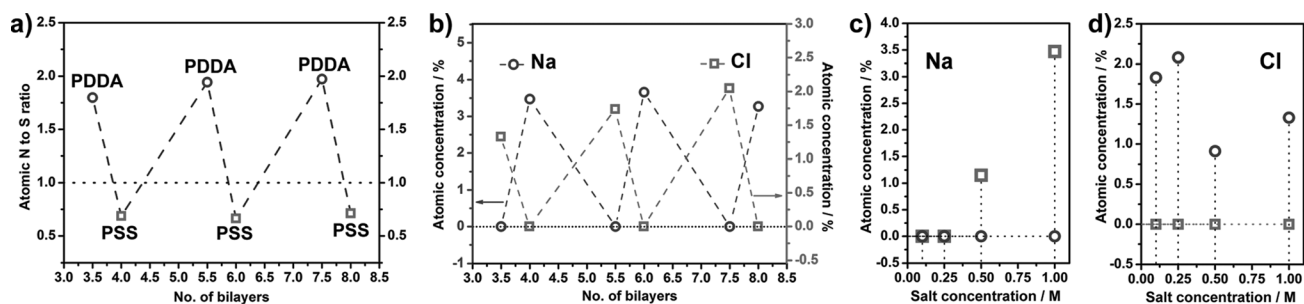
Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201411992>.

Surface wetting is conventionally studied in water-solid-air systems, and our study mainly focused on water-solid-oil systems because of the academic importance<sup>[4]</sup> and strong relevance in industry.<sup>[5]</sup> In this context, oil/water separation is an important technical application. To date, the prevailing strategy is to make hydrophilic nanostructures on the surfaces of separation membranes, inspired by the oil-repellent skins of fish and other aquatic organisms.<sup>[6]</sup> Such surface nanostructures are designed for water trapping, and can effectively offset the potential surface hydrophilicity loss because of their air-drying-induced surface reconstruction, thus ensuring underwater surface superoleophobicity. Here we discover that upon immersion into water, PSS-capped PEMs exhibit excellent oil-repellency regardless of aging treatment in air. This repellency has encouraged us to coat conventional steel meshes with PSS-capped PEMs, thus enabling highly efficient separation of water from oil/water mixtures at high flux, and opening promising prospects in the oil-water separation industry.

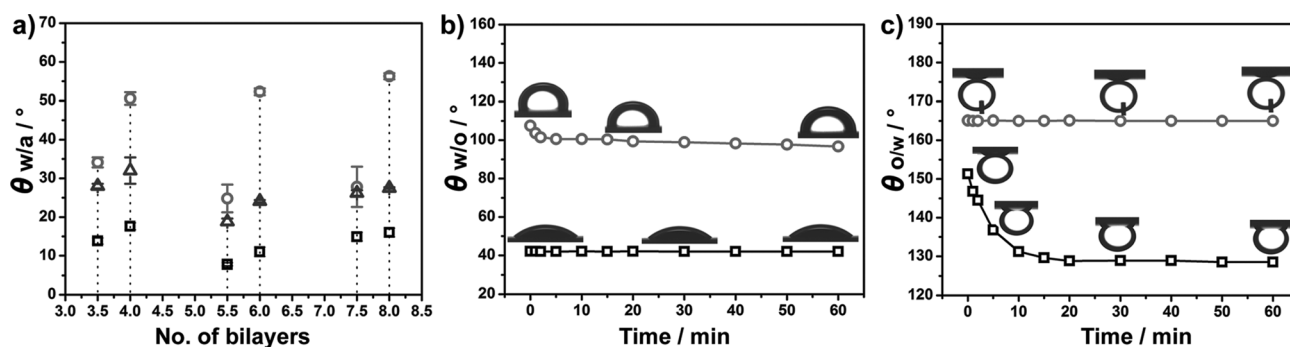
To date, a large variety of polyelectrolytes have been used to produce PEMs by LbL electrostatic deposition.<sup>[7]</sup> PDPA and PSS are the most commonly used, permanently charged polyelectrolytes. Here they were alternately deposited onto silicon wafers in the presence of 1.0 M NaCl and the resulting PEMs were denoted as (PDPA/PSS)<sub>*n*</sub>, where “*n*” represents the bilayer numbers. In this work, we mainly studied (PDPA/PSS)<sub>3.5</sub> and (PDPA/PSS)<sub>4.0</sub> PEMs with a surface roughness of less than 3 nm (see Figure S1 in the Supporting Information), so the impact of the surface roughness on surface wetting was ignored. The surface compositions of as-prepared (PDPA/PSS)<sub>*n*</sub> PEMs were examined by X-ray photoelectron spectroscopy (XPS; see Figure S2 and Table S1 in the Supporting Information). Figure 1a shows that the N to S atomic ratio is alternately switched from about 0.7 for PSS-capped PEMs to 1.7–2.0 for PDPA-capped PEMs. The type of the counterions present on the PEMs, determined by XPS, is indicative of the charge balance during alternating deposition of PDPA and PSS.<sup>[8]</sup> Figure 1b shows that the counterions of the QA<sup>+</sup> groups, Cl<sup>-</sup> ions, are detected exclusively on the PDPA-capped surfaces while the counterions of the BS<sup>-</sup> groups, Na<sup>+</sup> ions, are exclusively detected on the PSS-capped surfaces, thus indicating surface charge overcompensation during

alternating adsorption of PDPA and PSS. This observation, however, is different from the recent report of Schlenoff et al., in which the surface charge overcompensation was observed only for PDPA adsorption.<sup>[8]</sup> According to XPS measurements of (PDPA/PSS)<sub>*n*</sub> PEMs obtained at different NaCl concentrations (see Figure S3 and Table S2 in the Supporting Information),<sup>[9]</sup> we observe that the atomic concentration of Na<sup>+</sup> ions detected on the PSS-capped surfaces decreases from 3.5% to 1.3% with the NaCl concentrations used for LbL deposition decreasing from 1.0 to 0.5 M, and becomes undetectable when NaCl concentrations further reduce to 0.25 and 0.1 M (Figure 1c). In contrast, Cl<sup>-</sup> ions are clearly detected on all the PDPA-capped surfaces obtained at different NaCl concentrations (Figure 1d). Schlenoff et al. observed overcompensation upon PSS deposition at NaCl concentrations of greater than 1.5 M, and was attributed to NaCl-induced PEM plasticization.<sup>[8]</sup> While this plasticization could account for our results, here PSS overcompensation occurred at 0.5 M NaCl. A detailed study of the NaCl concentration effect on the amount of counterions detected on (PDPA/PSS)<sub>*n*</sub> PEMs, is underway.

From the XPS data, we estimated that 25–35% of the QA<sup>+</sup> groups and 70–80% of the BS<sup>-</sup> groups are uncompensated for on the (PDPA/PSS)<sub>3.5</sub> and (PDPA/PSS)<sub>4</sub> PEM surfaces obtained in 1.0 M NaCl. Figure 2a shows that the resulting PEMs can be readily wetted by water in air, with a  $\theta_{w/a}$  value of 15–20°, and is a result of the effective hydration of the surface ionic groups. After 72 hours of aging at 60°C in air, the  $\theta_{w/a}$  values increased to about 34° and 51° for (PDPA/PSS)<sub>3.5</sub> and (PDPA/PSS)<sub>4</sub> PEMs, respectively, thus suggesting that the surface hydrophilicity of the PSS capping is weaker and more vulnerable to air aging than the PDPA capping. When oil is utilized instead of air to challenge water wetting on the resulting PEMs, as shown in Figure 2b, the PDPA-capped surfaces remain easily wetted by water ( $\theta_{w/o} \approx 42^\circ$ ), while water wetting on the PSS-capped surfaces becomes noticeably poorer, with  $\theta_{w/o}$  decreasing from 110° to an equilibrium value of 97° over time. These results are inconsistent with the hydration strength of surface ionic groups. As suggested in the literature,<sup>[2d]</sup> the BS<sup>-</sup> groups (i.e., their SO<sub>3</sub><sup>-</sup> moieties) on PSS-capped surfaces are expected to be more strongly hydrated than the QA<sup>+</sup> groups on PDPA-capped



**Figure 1.** a) Plot of the N to S atomic ratios on (PDPA/PSS)<sub>*n*</sub> PEMs, prepared by LbL deposition in 1.0 M NaCl, versus the bilayer number. b) Plot of the atomic concentration of Na (circles) and Cl (squares) on (PDPA/PSS)<sub>*n*</sub> PEMs, prepared by LbL deposition in 1.0 M NaCl, versus the bilayer number. Plot of the atomic concentration of Na (c) and Cl (d) on PDPA- (circles) and PSS-capped (squares) surfaces versus the NaCl concentration used for LbL growth of (PDPA/PSS)<sub>*n*</sub> PEMs. In Figure c and d, (PDPA/PSS)<sub>3.5</sub> and (PDPA/PSS)<sub>4.0</sub> PEMs, obtained in 1.0 M NaCl, are compared with the PDPA-capped and PSS-capped PEMs, obtained in dilute NaCl, with similar thickness and roughness.<sup>[9]</sup> All the data are obtained from XPS measurements.



**Figure 2.** a) Plot of the  $\theta_{w/a}$  values of (PDDA/PSS) PEMs, which were freshly prepared (squares), aged for 72 hours at room temperature (triangles), and at 60°C (circles), versus the bilayer number. b,c) Temporal evolution profiles of the  $\theta_{w/o}$  (b) and  $\theta_{o/w}$  (c) values of (PDDA/PSS)<sub>3.5</sub> (squares) and (PDDA/PSS)<sub>4.0</sub> (circles) PEMs. The PEMs are prepared by LbL deposition in 1.0 M NaCl.

surfaces. Obviously, this inconsistency cannot be simply reconciled by surface reconstruction of the surface ionic groups upon contact with air or oil.

We also studied oil wetting on (PDDA/PSS)<sub>n</sub> PEMs. Oil can completely wet the (PDDA/PSS)<sub>n</sub> PEMs in air, with the oil contact angle in air ( $\theta_{o/a}$ ) at less than 5°. Figure 2c shows oil wetting on (PDDA/PSS)<sub>n</sub> PEMs in water. When the PEMs are brought in contact with a pendant droplet of hexadecane (2  $\mu$ L) in water, both (PDDA/PSS)<sub>3.5</sub> and (PDDA/PSS)<sub>4</sub> PEMs initially exhibit a  $\theta_{o/w}$  value above 150°. With the prolonged contact time, however, the  $\theta_{o/w}$  value of the PDDA-capped surfaces gradually drops from 152° to 133° within 20 minutes while that of the PSS-capped surfaces remains as high as 165° with no detectable change. When the PEMs were removed from the hexadecane droplet, the oil droplets stayed on the PDDA-capped surfaces (see Figure S4a and Movie S1 in the Supporting Information), whereas complete oil detachment was observed on the PSS-capped surfaces, even after the surfaces were kept in tight contact with the oil droplets for 12 hours (see Figure S4b and Movie S2 in the Supporting Information). This excellent oil repellency, however, was not found on the PSS-capped PEMs made by LbL deposition in 0.25 and 0.10 M NaCl; the oil droplet stably adhered to the surfaces despite the large  $\theta_{o/w}$  value (ca. 155°; see Figure S5 in the Supporting Information). Since complete compensation occurs upon PSS deposition in dilute NaCl solutions (Figure 1c), we believe that the above observed oil repellency of the PSS-capped PEMs prepared in 1.0 M NaCl arises from strong hydration of uncompensated BS<sup>-</sup> groups on the surfaces. Distinct from water wetting in air or oil, oil wetting in water is clearly consistent with the reported hydration strength of the ionic groups on the resulting PEMs.<sup>[2d]</sup>

Based on the Young equation, the  $\theta_{w/a}$ ,  $\theta_{o/a}$ ,  $\theta_{w/o}$ , and  $\theta_{o/w}$  of a solid surface are correlated by:

$$\cos\theta_{o/w} = (\gamma_{o/a}\cos\theta_{o/a} - \gamma_{w/a}\cos\theta_{w/a}) / \gamma_{o/w} \quad (1)$$

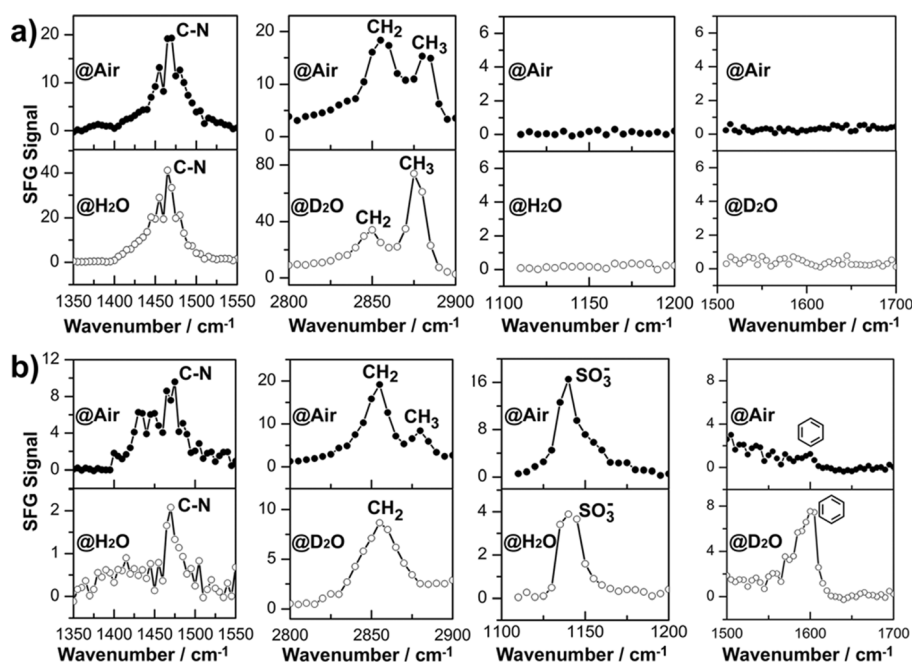
$$\theta_{o/w} + \theta_{w/o} = 180^\circ \quad (2)$$

where  $\gamma_{o/a}$ ,  $\gamma_{w/a}$ , and  $\gamma_{o/w}$  are the oil/air, water/air, and oil/water interfacial tensions, respectively. To simplify the calculation, we approximated that  $\theta_{o/a} = 5^\circ$  (for hexadecane) and  $\theta_{w/a} = 30^\circ$  for both (PDDA/PSS)<sub>3.5</sub> and (PDDA/PSS)<sub>4</sub> PEMs, values

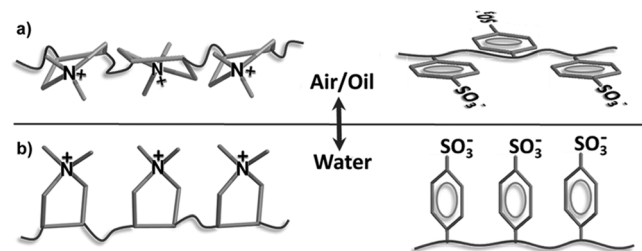
which are reasonable for the PEMs obtained after 72 hours of aging in air (Figure 2a). According to Equations (1) and (2),  $\theta_{o/w}$  and  $\theta_{w/o}$  are calculated to be 135° and 45°, respectively. These theoretical values are similar to the experimentally measured data of the (PDDA/PSS)<sub>3.5</sub> PEM ( $\theta_{o/w} = 133^\circ$  and  $\theta_{w/o} = 42^\circ$ ), but considerably smaller than those of the (PDDA/PSS)<sub>4</sub> PEM ( $\theta_{o/w} = 165^\circ$  and  $\theta_{w/o} = 97^\circ$ );  $\theta_{o/w} + \theta_{w/o} = 262^\circ (> 180^\circ)$ .<sup>[10]</sup>

To reveal the molecular rationale for their complicated wetting behavior, the surface molecular structures of the (PDDA/PSS)<sub>3.5</sub> and (PDDA/PSS)<sub>4</sub> PEMs, obtained by LbL deposition in 1.0 M NaCl, were investigated by sum frequency generation vibrational spectroscopy (SFG; Figure 3). SFG is an intrinsically surface-specific method which provides information about molecular conformation and orientation at various interfaces.<sup>[11]</sup> Figure 3a shows that in water the uncompensated QA<sup>+</sup> groups on the (PDDA/PSS)<sub>3.5</sub> PEMs exhibit fairly strong C–N<sup>+</sup> stretching vibrational signal, thus indicating the surface QA<sup>+</sup> groups preferentially orient perpendicular to the surface plane (Figure 4b). The strong CH<sub>3</sub> stretching signal in water suggests that each QA<sup>+</sup> group has two CH<sub>3</sub> moieties normal to the surface in direct contact with water (Figure 4b). The CH<sub>2</sub> stretching signal is also strong in water (compared to that in air), though weaker than the CH<sub>3</sub> one, thus indicating that the two CH<sub>2</sub> moieties of the pyrrolidine ring are also ordered on the surface and directly in contact with water.<sup>[12]</sup> This orientational configuration agrees with the molecular structures of the surface QA<sup>+</sup> groups where the N<sup>+</sup> center isotropically enveloped by two CH<sub>3</sub> and two CH<sub>2</sub> moieties in each pyrrolidine ring (see Scheme S1), and accounts for the wetting behavior of the PDDA-capped surface in water. This alkyl envelopment greatly lowers the hydration effectiveness of the N<sup>+</sup> center and, at the same time, facilitates oil adhesion on the PDDA-capped surface in water. When the PDDA-capped surface is exposed to air, the CH<sub>3</sub> stretching signal becomes weaker than that of CH<sub>2</sub> (Figure 3a), thus indicating that the surface QA<sup>+</sup> groups orient parallel to the surface plane with two CH<sub>2</sub> moieties of the pyrrolidine ring protruding more from the surface plane than the two CH<sub>3</sub> moieties (Figure 4a). This orientation change may just slightly change the surface area occupied by each QA<sup>+</sup> group and in turn the surface charge density on the PDDA capped surface, because quaternized pyrrolidine rings





**Figure 3.** SFG spectra of (PDDA/PSS)<sub>3.5</sub> (a) and (PDDA/PSS)<sub>4.0</sub> (b) PEMs measured in air (upper panel) and water (lower panel). The PEMs were produced by LbL deposition in 1.0 NaCl. Deuterated water is used instead of water to distinctly reveal the vibration signal of alkyl and phenyl moieties.



**Figure 4.** Schematic illustration of the orientational configuration of the uncompensated QA<sup>+</sup> groups on (PDDA/PSS)<sub>3.5</sub> PEMs and the uncompensated BS<sup>-</sup> groups on (PDDA/PSS)<sub>4.0</sub> PEMs in response to the surrounding environmental change.

are inserted as bulky repeating units in the PDDA backbone and the N<sup>+</sup> center of each ring is enveloped by two CH<sub>3</sub> and two CH<sub>2</sub> moieties. The distinct C–N<sup>+</sup> stretching signal in air, albeit weaker than that in water, indicates that the surface QA<sup>+</sup> groups point the N<sup>+</sup> centers towards air, and facilitates the surface hydration. Hence the surface charge density on the PDDA-capped surfaces is little altered and, therefore, the water wetting remains effective regardless of the orientation of the surface QA<sup>+</sup> groups in response to the environmental change.

Figure 3b shows that the SO<sub>3</sub><sup>-</sup> moieties of the uncompensated BS<sup>-</sup> groups on the (PDDA/PSS)<sub>4</sub> PEMs are present both in air and water, but the aromatic C=C stretching signal of the Ph moieties appears only in water, thus indicating the different orientation and ordering of the Ph moieties in air and water. Since surface BS<sup>-</sup> groups have the SO<sub>3</sub><sup>-</sup> and Ph moieties placed side by side (see Scheme S1), and when their Ph moieties orient perpendicular to the surface plane with

ordering in water, individual surface BS<sup>-</sup> groups on the PSS-capped surfaces will occupy minimal surface area (Figure 4b), thus maximizing the surface charge density and transforming the strong surface hydration of the SO<sub>3</sub><sup>-</sup> moieties into strong oil repellency in water. In air, however, the Ph moieties randomly orient parallel to the surface plane, so the surface area occupied by each surface BS<sup>-</sup> group is maximized (Figure 4a), thus significantly reducing the surface charge density and in turn the surface hydrophilicity. This arrangement explains the poor water wetting on PSS-capped surfaces in oil/air.

Whereas neither SO<sub>3</sub><sup>-</sup> nor Ph moieties of BS<sup>-</sup> groups are visible in the SFG spectra collected from the (PDDA/PSS)<sub>3.5</sub> PEM, the C–N<sup>+</sup> and CH<sub>3</sub> signals of the QA<sup>+</sup> groups were detected in the SFG spectra of the (PDDA/PSS)<sub>4</sub> PEM (Figure 3b). This detection implies that despite the surface charge overcompensation

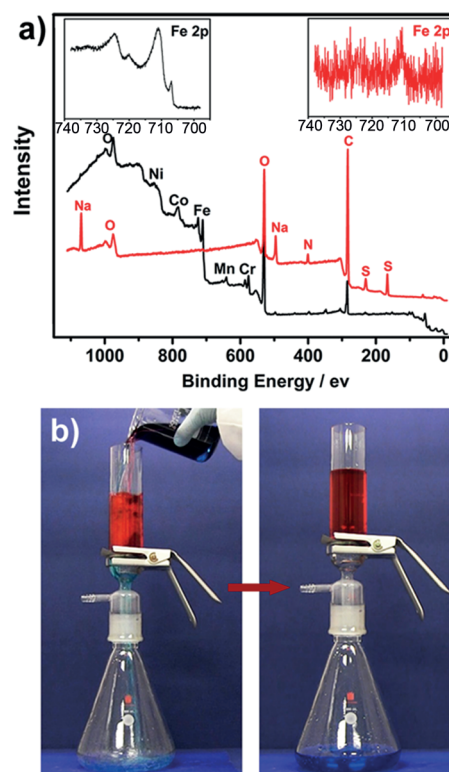
upon PSS adsorption in 1.0 M NaCl, a small number of the QA<sup>+</sup> groups from the PDDA layer beneath, as evidenced by their weaker intensities compared to those observed on the PDDA-capped PEM surface, remain exposed to the environment, along with the BS<sup>-</sup> groups of the PSS capping. This finding inspired us to focus on understanding the internal structure of (PDDA/PSS)<sub>n</sub> PEMs, as it is still under debate. Figure 3b indicates the absence of the CH<sub>3</sub> stretching vibration signal of QA<sup>+</sup> groups in water, and it is reasonable when the surface BS<sup>-</sup> groups stand up on the surfaces in water, and is clearly beneficial for the PSS-capped surfaces to keep hydrated and repel oil in water.

According to literature,<sup>[13]</sup> counterions are expected to be strongly bound with the surface ionic groups on as-prepared (PDDA/PSS)<sub>n</sub> PEMs through electrostatic interactions and in turn affect the surface wetting behavior. To study the counterion effect, the counterions of the surface QA<sup>+</sup> groups were changed from Cl<sup>-</sup> to Br<sup>-</sup> ions by adsorption of the outmost PDDA layer in 1.0 M NaBr and the counterions of the surface BS<sup>-</sup> groups from Na<sup>+</sup> to K<sup>+</sup> ions by adsorption of the outmost PSS layer in 1.0 KCl (see Figure S6 and Table S3 in the Supporting Information).<sup>[14,15]</sup> The counterion nature is found to noticeably affect  $\theta_{w/a}$  values of the resulting PEMs according to the Hofmeister series<sup>[2a,b]</sup> (see Figure S7a in the Supporting Information), while its impact on their  $\theta_{w/o}$  value is clearly dependent on the surface ionic group nature (see Figure S7b). With the counterion polarizability increasing from Cl<sup>-</sup> to Br<sup>-</sup> ions and from Na<sup>+</sup> to K<sup>+</sup> ions,<sup>[2a,b]</sup> the  $\theta_{w/o}$  value noticeably increases for the PDDA capping while it is little changed for the PSS capping. Further, the  $\theta_{o/w}$  value of the PEMs is hardly affected by the counterion nature (see Figure S7c). Taken together, water (de-)wetting on (PDDA/

PSS)<sub>n</sub> PEMs ought to be more significantly correlated with the surface ionic group nature.

We also capped (PDDA/PSS)<sub>n</sub> PEMs with poly(allylamine) (PAH) and poly(acrylic acid) (PAA) in the presence of 1.0 M NaCl.<sup>[14]</sup> Neither PAH nor PAA capping is oil-repellent (see Figure S7c), which implies that the PAH and PAA chains capped on the PEMs readily orient their hydrophobic moieties or backbones towards oil. This orientation is reasonable considering the small monomer volumes of PAH and PAA compared with those of PSS and PDDA (see Scheme S1). The PAH capping displays rather large  $\theta_{w/a}$  and  $\theta_{w/o}$  values (see Figure S7). This poor water wetting hints that the reconstruction of the surface allylamine groups in air or oil significantly reduces the surface charge density of the PAH capping, and is in line with the anisotropic configuration of the allylamine groups, similar to the BS<sup>-</sup> groups of PSS, in which their CH<sub>2</sub> and NH<sub>3</sub><sup>+</sup> moieties are well separated. In contrast, the PAA capping is readily wetted by water with small  $\theta_{w/a}$  and  $\theta_{w/o}$  values, and is comparable to those of the PDDA capping (see Figure S7). This behavior can be assigned to the fact that the COO<sup>-</sup> groups of PAA, similar to the QA<sup>+</sup> groups of PDDA, are directly linked to the backbones so the orientation of the surface COO<sup>-</sup> group may just slightly change the surface charge density. Thus, these results further corroborate the strong correlation of the surface wetting behavior of PEMs with the surface ionic group nature.

After the surface reconstruction in air, hydrophilic surfaces are usually hard to restore their original hydrophilicity even by immersion in water.<sup>[16]</sup> Because of the high flexibility of the PEMs obtained by LbL deposition,<sup>[15]</sup> PSS-capped PEMs were found to be capable of retaining the superior oil-repellency immediately after immersion in water, regardless of the post aging treatment (see Figure S8 in the Supporting Information). Encouraged by that, we coated stainless steel meshes with apertures of 25  $\mu\text{m}$  by (PDDA/PSS)<sub>n</sub> PEMs through LbL deposition in 1.0 M NaCl. Since the oil-repellency performance is independent on the layer number (see Figure S9 in the Supporting Information), smooth (PDDA/PSS)<sub>4</sub> PEMs were used for the mesh coating, which are thick enough to fully cover the mesh surface as evidenced by the disappearance of metal signals in XPS spectra (Figure 5a). The resulting meshes allow easy filtration of water from an oil/water mixture at high water flux of about 610 L m<sup>-2</sup> s<sup>-1</sup> (Figure 5b and see Movie S3 in the Supporting Information) with high separation efficiency; oil is barely detected in the filtrated water (see Figure S10 in the Supporting Information). The surface roughness of the (PDDA/PSS)<sub>4</sub> coating is less than 3 nm (see Figure S1b), and the notches and scratches present on the steel meshes are on the scale of tens to hundreds of micrometers (see Figure S11 in the Supporting Information). Thus, the contribution of the surface roughness to the high oil/water separation efficiency can be ignored. Since the (PDDA/PSS)<sub>4</sub> coating were produced by LbL deposition in 1.0 M NaCl, its superior oil-repellency in water exhibited long term stability against acid, alkaline, and salt at high concentrations, and will be advantageous for technical applications such as oil-spill cleanup on seawater.



**Figure 5.** a) XPS wide scan spectra of a stainless steel mesh with (red) and without (black) (PDDA/PSS)<sub>4</sub> PEMs coated atop by LbL deposition in 1.0 M NaCl. The insets show the corresponding high-resolution spectra of Fe in the steel mesh. b) Photos shot during filtration of the mixtures of hexadecane, stained by Oil Red O, and water, stained by methylene blue, through a (PDDA/PSS)<sub>4</sub>-coated stainless steel mesh (left panel) and after the filtration (right panel), in which water is selectively filtered through the steel mesh while hexadecane is retained on the top of the mesh. The aperture of the steel mesh is 25  $\mu\text{m}$ .

In summary, we demonstrate a prominent impact of the nature of the surface ionic group on the surface wetting behavior of (PDDA/PSS)<sub>n</sub> PEMs, and it hinges mainly on the configurational geometry of the uncompensated ionic groups on the surfaces. For PDDA-capped surfaces, the orientation of the surface QA<sup>+</sup> groups with isotropic configuration with respect to the surface plane hardly affect the surface hydrophilicity. For PSS-capped surfaces, the strong hydration of surface BS<sup>-</sup> groups with anisotropic configuration can be translated either into excellent oil-repellency in water (poor water de-wetting) or to poor water wetting (in air or oil) depending on the orientational order and directionality of the BS<sup>-</sup> groups with respect to the surface plane. This configurational effect should be a better framework to interpret the wetting behavior of a charged surface according to the molecular nature of surface ionic groups. We hope it will stimulate studies to revisit experimental and theoretical molecular design of surface wetting,<sup>[17]</sup> and that research will focus more on the molecular features of the substituents next to the ionic centers of surface groups, features such as size, shape, flexibility, and spatial arrangement with regard to the ionic centers rather than simply on the hydration strength of the ionic centers alone.

Further, the lessons learnt from correlation of the surface wetting behavior of PEMs, obtained by LbL deposition, with their surface local structures will shed light on the study of the PEM internal structures, which is still under debate. Thanks to the operational simplicity and versatility of LbL deposition, our success in using (PDDA/PSS)<sub>4</sub>-coated meshes for efficient oil-water separation also endorses the technical significance of PEMs in self-cleaning applications.

**Keywords:** interfaces · oil-water separation · photoelectrospectroscopy · structure elucidation · surface chemistry

**How to cite:** *Angew. Chem. Int. Ed.* **2015**, *54*, 4851–4856  
*Angew. Chem.* **2015**, *127*, 4933–4938

- [1] a) J. Israelachvili, H. Wennerstrom, *Nature* **1996**, *379*, 219–225; b) U. Raviv, S. Giasson, N. Kampf, J.-F. Gohy, R. Jerome, J. Klein, *Nature* **2003**, *425*, 163–165.
- [2] a) K. D. Collins, *Biophys. J.* **1997**, *72*, 65–76; b) W. Kunz, P. Lo Nostro, B. W. Ninham, *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 81–91; c) L. B. Sagle, K. Cimat, V. A. Litosh, Y. Liu, S. C. Flores, X. Chen, B. Yu, P. S. Cremer, *J. Am. Chem. Soc.* **2011**, *133*, 18707–18712; d) R. Scheu, Y. Chen, H. B. de Aguiar, B. M. Rankin, D. Ben-Amotz, S. Roke, *J. Am. Chem. Soc.* **2014**, *136*, 2040–2047.
- [3] N. Giovambattista, P. G. Debenedetti, P. J. Rossky, *J. Phys. Chem. B* **2007**, *111*, 9581–9587.
- [4] M. Ramiasa, J. Ralston, R. Fetzer, R. Sedev, D. M. Fopp-Spori, C. Morhard, C. Pacholski, J. P. Spatz, *J. Am. Chem. Soc.* **2013**, *135*, 7159–7171.
- [5] D. N. Rao, *Colloids Surf. A* **2002**, *206*, 203–216.
- [6] a) M. Liu, S. Wang, Z. Wei, Y. Song, L. Jiang, *Adv. Mater.* **2009**, *21*, 665–669; b) Y. C. Jung, B. Bhushan, *Langmuir* **2009**, *25*, 14165–14173.
- [7] a) *Multilayer Thin Films* (Eds.: G. Decher, J. Schlenoff), Wiley-VCH, Weinheim, **2003**; b) J. F. Quinn, A. P. R. Johnston, G. K. Such, A. N. Zelikin, F. Caruso, *Chem. Soc. Rev.* **2007**, *36*, 707–718; c) Z. Y. Tang, Y. Wang, P. Podsiadlo, N. A. Kotov, *Adv. Mater.* **2006**, *18*, 3203–3224; d) J. Sun, T. Wu, Y. Sun, Z. Wang, X. Zhang, J. Shen, W. Cao, *Chem. Commun.* **1998**, 1853–1854.
- [8] R. A. Ghostine, M. Z. Markarian, J. B. Schlenoff, *J. Am. Chem. Soc.* **2013**, *135*, 7636–7646.
- [9] Note that (PDDA/PSS)<sub>5,5</sub> and (PDDA/PSS)<sub>6,0</sub> were produced by LbL deposition in 0.50 M NaCl, (PDDA/PSS)<sub>9,5</sub> and (PDDA/PSS)<sub>10,0</sub> PEMs in 0.25 M NaCl and (PDDA/PSS)<sub>14,5</sub> and (PDDA/PSS)<sub>15,0</sub> PEMs in 0.10 M NaCl, the thickness and surface roughness of which were comparable to that of (PDDA/PSS)<sub>3,5</sub> and (PDDA/PSS)<sub>4,0</sub> PEMs.
- [10] Note that using the experimental  $\theta_{wa}$  value (52°) of the (PDDA/PSS)<sub>4</sub> PEMs obtained after 72 hours of aging at 60°C, the  $\theta_{ow}$  and  $\theta_{wo}$  values were calculated at 112° and 68°, respectively, by using Equations (1) and (2), and they were still significantly smaller than experimental values.
- [11] Z. Chen, *Prog. Polym. Sci.* **2010**, *35*, 1376–1402.
- [12] Note that the CH<sub>2</sub> moieties of the PDDA backbone should have a small contribution to the CH<sub>2</sub> stretching vibration signal as they may be either shielded by the pyrrolidine ring of the QA<sup>+</sup> groups or randomly oriented within the surface plane (Figure 4).
- [13] a) F. Zhang, Z. Ali, F. Amin, A. Feltz, M. Oheim, W. J. Parak, *ChemPhysChem* **2010**, *11*, 730–735; b) A. Riedinger, F. Zhang, F. Dommershausen, C. Röcker, S. Brandholt, G. U. Nienhaus, U. Koert, W. J. Parak, *Small* **2010**, *6*, 2590–2597.
- [14] The use of different electrolyte and polyelectrolytes for LbL deposition can yield PEMs with different surface morphology, surface charge, and internal structure (Ref [15]). To avoid that technical issue, new electrolytes and polyelectrolytes were used only for growth of the outmost layers rather than the entire PEMs. (PDDA/PSS)<sub>3,0</sub> and (PDDA/PSS)<sub>3,5</sub> PEMs, obtained in 1.0 M NaCl, were used for deposition of polycations and polyanions in 1.0 M salt, respectively, so the resulting PEMs should be comparable to (PDDA/PSS)<sub>3,5</sub> and (PDDA/PSS)<sub>4,0</sub> PEMs obtained in 1.0 M NaCl in terms of the film thickness and surface morphology and charge.
- [15] R. von Klitzing, *Phys. Chem. Chem. Phys.* **2006**, *8*, 5012–5033.
- [16] T. Serizawa, S. Hashiguchi, M. Akashi, *Langmuir* **1999**, *15*, 5363–5368.
- [17] a) A. Ulman, *Chem. Rev.* **1996**, *96*, 1533–1554; b) A. Y. Fadeev, T. J. McCarthy, *Langmuir* **1999**, *15*, 3759–3766.

Received: December 14, 2014

Revised: January 21, 2015

Published online: February 20, 2015