

Supporting Material

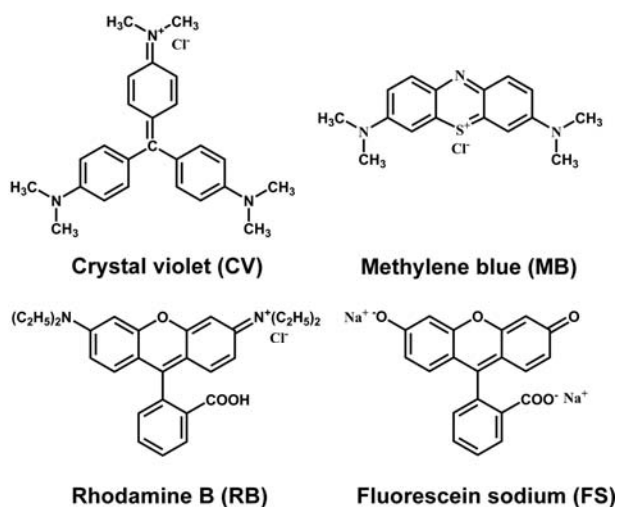
**Layer-by-Layer Deposition of Polyelectrolyte Complexes for the Fabrication of
Foam Coatings with High Loading Capacity**

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Materials. Poly(diallyldimethylammonium chloride) (PDDA, 20 wt %, *Mw* ca. 100 000-200 000), poly(acrylic acid) (PAA, *Mw* ca. 100,000), and poly(sodium 4-styrenesulfonate) (PSS, *Mw* ca. 70 000) were purchased from Sigma-Aldrich. All chemicals were used without further purification. Diazo-resin (DAR) was synthesized according to a literature procedure.¹ The molecular weight (*Mn*) of the DAR was ~2640. Deionized water was used for all the multilayer fabrication. The dyes of crystal violet, methylene blue, rhodamine B and fluorescein sodium were purchased from Beijing Chemical Reagents Company. Their chemical structures are shown in Scheme S1.



Scheme S1. Chemical structures of various dyes used in this work.

Characterization. UV-vis absorption spectra were recorded on a Shimadzu

UV-2550 spectrophotometer. Dynamic light scattering (DLS) studies and ζ -potential measurements were carried out on a Malvern Nano-ZS zetasizer at room temperature. The measurements were made at a scattering angle of $\theta = 173^\circ$ at 25 °C using a He-Ne laser with a wavelength of 633 nm. Scanning electron microscopy (SEM) images were obtained on a XL30 ESEM FEG field emission scanning electron microscope.

Preparation of PAA-DAR and DAR-PSS Complexes. The negatively charged PAA-DAR complexes were prepared by dropwise adding 1mg mL⁻¹ DAR to the solution of 1mg mL⁻¹ PAA under intensive stirring to make the feed monomer molar ratio of PAA to DAR being 9:1. In the same way, cationic polyelectrolyte complexes of DAR-PSS with a feed monomer molar ratio of DAR to PSS being 3:1 were prepared by dropwise mixing 1mg mL⁻¹ DAR with 1mg mL⁻¹ PSS under intensive stirring. The aqueous PAA-DAR and DAR-PSS dispersions were finally adjusted to pH 3.5 with addition of either diluted NaOH or HCl. The sizes of the PAA-DAR and DAR-PSS complexes were characterized by DLS measurements. As shown in Fig. S1a and b, PAA-DAR and DAR-PSS complexes exhibit a polydisperse but monomodal distribution with an average hydrodynamic diameter of ~178 and ~125 nm, respectively.

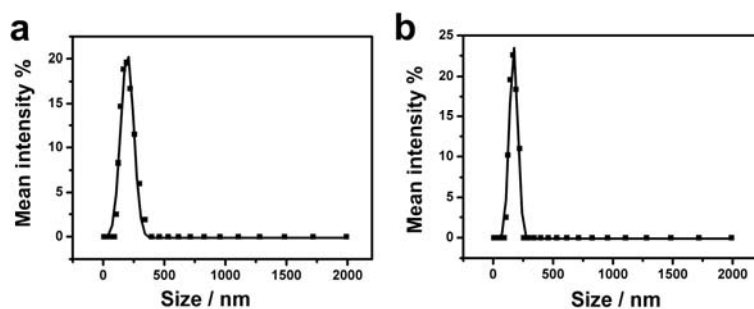
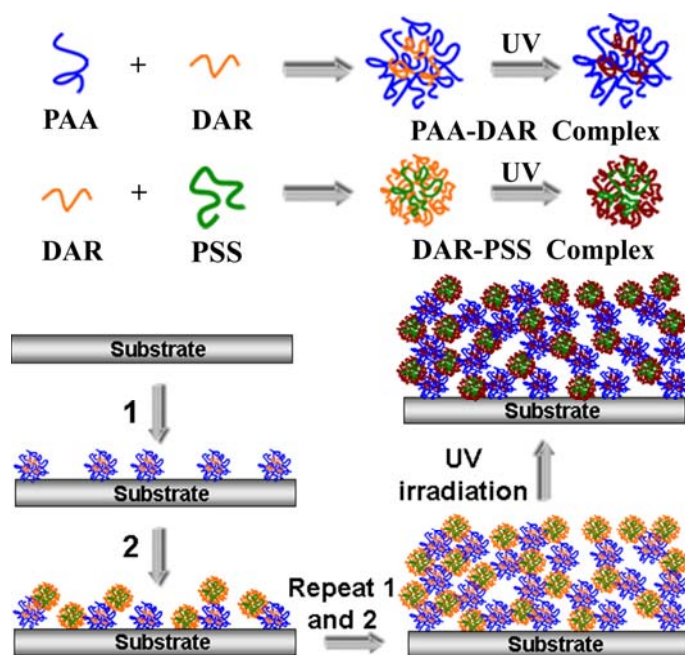


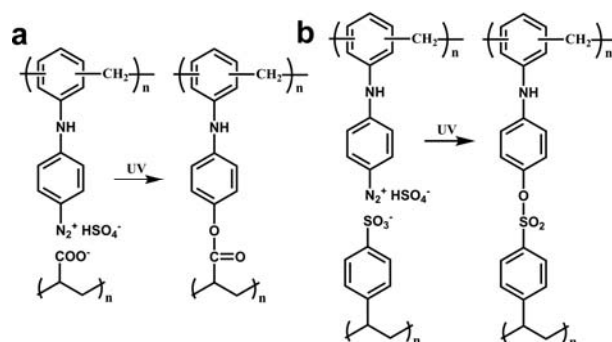
Fig S1 Hydrodynamic diameter distribution curves of PAA-DAR (a) and DAR-PSS (b) complexes in aqueous dispersion at pH 3.5, respectively.

Foam Coating Preparation. Quartz and silicon wafers were immersed in piranha solution (1:3 mixture of 30% H₂O₂ and 98% H₂SO₄) and heated until no bubbles were released. *Caution: Piranha solution reacts violently with organic material and should be handled carefully.* The LbL deposition of

PAA-DAR/DAR-PSS films was conducted in the dark automatically by a programmable dipping machine (Dipping Robot DR-3, Riegler & Kirstein GmbH), as schematically shown in Scheme S2. The cleaned quartz and silicon wafers were first immersed in PDDA aqueous solution (1.0 mg mL^{-1}) for 20 min to obtain a cationic ammonium-terminated surface. Then, the substrate was immersed into an aqueous dispersion of PAA-DAR (pH 3.5) for 20 min to obtain a layer of PAA-DAR complexes followed by rinsing with water (pH 3.5) three times for 2, 2 and 1min. Then the substrate was transferred to an aqueous dispersion of DAR-PSS for 20 min to obtain a layer of DAR-PSS complexes followed by rinsing with water (pH 3.5) three times for 2, 2 and 1min. The deposition of PAA-DAR and DAR-PSS layers were repeated until the desired layer number was reached. No drying step was used in the deposition procedure unless it was in the last layer. Finally, the photo-cross-linking of the PAA-DAR/DAR-PSS coatings was conducted by irradiating the coatings with a 250 W UV lamp at a distance of 10 cm from the source for 30 min to ensure that the reaction proceeds completely (5 min for each time to prevent the films from high temperature). The photo-reactions in the foam coatings are shown in Scheme S3.²



Scheme S2. Layer-by-layer deposition process for the fabrication of PAA-DAR/DAR-PSS foam coatings. The real situation for film fabrication might be more complicated than depicted here.



Scheme S3. Photoreactions of DAR with PAA (a) and PSS (b).

Influence of Drying Steps on Film Fabrication. Thin and compact films can be fabricated if drying steps are performed after each layer deposition during the LbL deposition of PAA-DAR/DAR-PSS coatings. The preparation process of the PAA-DAR/DAR-PSS coatings with drying steps was similar to that for PAA-DAR/DAR-PSS foam coatings as described in Scheme S2, except that a drying step using N_2 flow was performed after the substrate was washed in water. The cross-sectional and top-view SEM images of a (PAA-DAR/DAR-PSS)*15 coating LbL deposited with a drying step are shown in Fig. S2. The coating has a rather thin and compact structure as compared to its corresponding film fabricated without drying steps. The (PAA-DAR/DAR-PSS)*15 has an average thickness of 134 ± 30 nm with one bilayer of PAA-DAR/DAR-PSS being 9 ± 2 nm. This value is much smaller than that of the coatings fabricated without drying steps. N_2 drying step can produce a lateral force for the spread of PAA-DAR and DAR-PSS complexes and remove most of the hydrated water in PAA-DAR and DAR-PSS complexes. As a result, the sphere-like complexes particles collapsed and spread to form a relatively compact film when deposited on the substrate. Therefore, LbL deposition without drying steps is critical to fabricate thick macroporous PAA-DAR/DAR-PSS foam coatings.

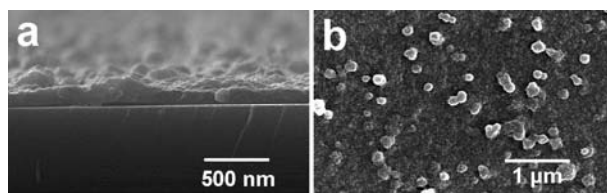


Fig S2 Cross-sectional (a) and top-view (b) SEM images of a (PAA-DAR/DAR-PSS)*15 coating fabricated with N_2 drying after each layer deposition.

Calculation of the Adsorption Capacity (Q_e) of the Foam Coatings. The Q_e of the foam coatings can be calculated by equation:

$$Q_e = (C_0 - C_e) V/m \quad (1)$$

herein, m is the mass of the coatings which were obtained by weighting the mass of the quartz before and after foam coating deposition. A (PAA-DAR/DAR-PSS)*20 coating deposited on both sides of a quartz slide ($15 \times 40 \text{ mm}^2$) has an average mass of 2.35 mg (averaged by 5 samples). C_0 is the original concentration of the aqueous dye solution, C_e is the equilibrium concentration of the dye solution after the saturation loading of dyes into the foam coatings. V is the volume of the aqueous dye solution. C_e is determined by the calibration curve of the dyes in aqueous solution.

Thickness-Dependent Loading of Dyes in Foam Coatings. UV-irradiated PAA-DAR/DAR-PSS coatings with different deposition cycles were immersed in a 15 mL RB solution with the initial concentration of $50 \mu\text{M}$ respectively to examine their loading behaviors. As shown in Fig. S3, the final concentration of the RB solution decreased with increasing number of the deposition cycles of the foam coating, indicating that thicker foam coatings have a higher loading amount of dyes. The result affirmatively confirms that dye molecules are loaded within the whole PAA-DAR/DAR-PSS coatings, but not limited to the surface of the coatings.

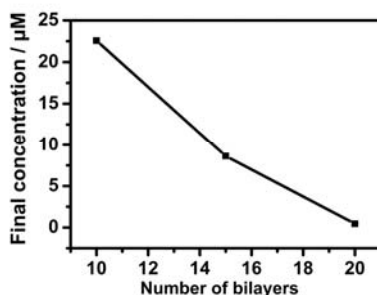


Fig. S3 Final equilibrium concentration of RB solution after adsorbed by the UV-irradiated PAA-DAR/DAR-PSS coatings with different deposition cycles.

Separation of Oppositely Charged Dyes. UV-irradiated PAA-DAR/DAR-PSS foam coating can selectively remove positively charged dyes when oppositely charged dyes co-exist in solution. A (PAA-DAR/DAR-PSS)*20 coating was immersed into a 15mL mixture solution containing $10 \mu\text{M}$ RB and $30 \mu\text{M}$ fluorescein sodium (FS) for

24 h. As shown in Fig. S4a, RB was selectively removed by the coating, and the color of the solution turned from orange red to green, which is the color of pure FS solution. UV-vis absorption spectra in Fig. S4b indicate that the absorption peak of RB at 554 nm can not be observed after 24 h adsorption. Meanwhile, the absorbance of the negatively charged FS at 488 nm decreases slightly. The overlap of the absorbance of RB and FS in the range of 400 to 600 nm accounts for the decrease of the FS absorbance in the UV-vis absorption spectrum after RB removal. Meanwhile, the interaction between RB and FS would result in co-adsorption of RB and FS molecules. Actually, the adsorption of negatively charged FS is significantly lower than that of the positively charged RB. The present result indicates that the UV-irradiated PAA-DAR/DAR-PSS foam coatings can be used for dye separation. The separation and purification of materials with larger dimensions than organic dyes such as proteins by the macroporous foam coatings is currently under investigation.

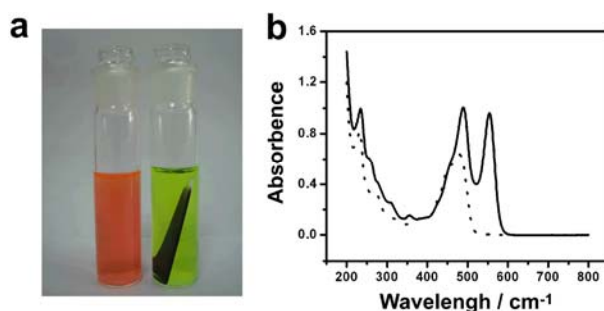


Fig. S4 (a) Photographs of a mixed solution of 10 μM RB and 30 μM FS before (left) and after (right) removal of RB by a (PAA-DAR/DAR-PSS)*20 coating. (b) UV-vis absorption spectra of the mixed solution before (solid line) and after (dotted line) RB removal.

References

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- 2 J. Q. Sun, W. Tao, Y. P. Sun, Z. Q. Wang, X. Zhang, J. C. Shen, and W.X. Cao, *Chem. Commun.*, 1998, 1853-1854. J. Q. Sun, T. Wu, F. Liu, Z.Q. Wang, X. Zhang and J. C. Shen, *Langmuir*, 2000, **16**, 4620-4624.