Supporting Information

Omniphobic Slippery Coatings Based on Lubricant Infused Porous Polyelectrolyte Multilayers

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Supplementary materials:

Materials and Methods

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**Materials and Methods**

**Materials.** Branched poly(ethyleneimine) (BPEI, MW = 25,000) was obtained from Sigma-Aldrich and poly(acrylic acid) (PAA, MW=50, 000, 25 wt% solution) was purchased from Polysciences Inc. Silica (20 nm and 4 nm) colloidal dispersions were purchased from Alfa Aesar. 1H, 1H, 2H, 2H-Perfluorooceryltriethoxysilane (POTS) was purchased from Sigma-Aldrich. The perfluoropolyether lubricant (Dupont Krytox PFPE GPL 100) was obtained from Miller-Stephenson and n-decane from TCI. De-ionized (DI) water with 18.2 MΩ resistivity from a Milli-Q filtration system was used for all experiments. All materials were used as received without further purification.

**Characterization.** Film thickness was measured using a stylus profilometer (KLA Tencor Instruments P6), and values reported represent an average of 5 different position of the film. Scanning electron microscopy (SEM) images were acquired using an FEI Quanta 600 field emission scanning electron microscope with an accelerating voltage of 10 kV. FTIR spectra were obtained using an IR Prestige 21 system (Shimadzu Corp., Japan) and analyzed by IRsolution V.1.40 software. Films coated on the silicon wafer were measured via attenuated total reflection (ATR) mode. Both the contact angle and photograph of droplets sliding on the surfaces were taken using VCA optima (AST products) equipped with tilting stage and the video camera.

**Polyelectrolyte Multilayer (PEM) Assembly.** PEMs were assembled onto glass slides, silicon wafers and a glass tube. Before use, the silicon wafer and glass substrates were treated in a freshly prepared piranha solution (mixture of H₂SO₄ (98%) and H₂O₂ (30%) with the volume ration v/v=7/3) at room temperature for 4 h and rinsed with DI water until neutralized. The substrates were then dried by nitrogen steam before being used for layer-by-layer assembly.
BPEI/PAA multilayer films were assembled using concentrations of 40 mmol/L BPEI and 20 mmol/L PAA with respect to the functional group (either amine groups or carboxylic acid). The pH of these solutions was adjusted with 1 mol/L NaOH or 1 mol/L HCl solution as needed. All the multilayer assembly was carried out at room temperature using a Zeiss HMS series programmable slide stainer. The cleaned and dried substrates were first exposed to BPEI solution for 10 min followed by three separate DI water rinse baths. Then, the substrates are exposed to PAA solution for 10 min and then again to three DI water rinse baths. This cycle was repeated until 30 bilayers were reached. The multilayer films are dried at room temperature for 24 hours before any testing.

**Introducing Porous Structure.** The films assembled on glass slides with 30 bilayers of BPEI/PAA were exposure to post-assembly acidic treatments. The DI water was adjusted to the desired pH using 1 mol/L NaOH or 1 mol/L HCl. PEM samples of defined dimension (1.25 cm×5 cm) and 14 ml of solutions were placed in a centrifuge tube for 1 hour. The staged acid etching was performed in a similar method. The 30 bilayer BPEI/PAA PEMs were immersed in pH 2.7 and then pH 2.3 for defined time intervals. After the film was air dried, it was crosslinked at 180 °C for 2 hours.

**Preparation of PFPE-infused Nano-textured Porous Structure.** Three bilayers of BPEI/silica particles (0.06wt% mixing dispersion of 20 nm and 4 nm silica particles in 1:1 ratio) were deposited on to the crosslinked porous multilayer film with the pH values of both the BPEI solution and the silica particle dispersion fixed at pH 6.5.

The silane treatment was carried out by chemical vapor deposition of POTS in a close-capped weighting bottle. 100 µL of POTS in a 2 mL vial and the crosslinked film were put into the
close-capped weighting bottle. The silanization reaction was performed at 120°C for 3 hours. After the CVD step the film was placed under vacuum for 1 h in order to ensure that all unbound silane was removed from the film. One hundred µL of PFPE lubricant was impregnated into the nano-textured porous film through spin coating at 2000 rpm for 1 min.

**Charge Density of Polyelectrolyte in the solution and in the film.**

![Image](image.png)

**Figure S1.** Dependence of film thickness of (BPEI/PAA)₃₀ PEMs on pH of BPEI solution. The concentration of BPEI and PAA are fixed as 40 mmol/L and 20 mmol/L with respect to the functional group (either carboxylic acid or amine group). The pH of PAA was chosen as 4.5. The polyelectrolyte charge densities and their conformation influence the overall film thickness.
Figure S2. Degree of Ionization of BPEI in solution as a function of pH. BPEI concentration was fixed at 40 mmol/L of polymer amine functional groups, which is the same as the assembly solution. The degree of ionization increases to 60% with decreasing the pH value.

For weak polyelectrolytes such as BPEI or PAA, the degree of ionization can be altered by a small adjustment of pH of assemble solution which influences both the film thickness and multilayer architecture. As shown in figure S2, the degree of ionization can increase to as high as 60% with decreasing pH value. Since BPEI becomes less charged as pH increases to 9.5, the chains become more coiled, the LbL film has less PAA, and those PAA chains have a high degree of ionization due to their interaction with BPEI as shown in figure S3. The resulting film has many tails and loops and deposits as thick layers (figure S1). A higher degree of ionization (low assemble pH) on the BPEI chains, however, results in thinner layers. During immersion in solutions of different pH values for 1 hour, the ionic densities of both polymers is changed, and above or below certain pH ranges the film changes in morphology and eventually dissolves. Our
data indicates that films where the coil conformations were extended will dissolve more readily, possibly due to less entanglement and diffusion of film components.

**Figure S3.** Degree of ionization of PAA in dried (BPEI/PAA)$_{30}$ films after immersion in films of different pH values for 1 hr. Ionization is determined from the FTIR spectra of these films. The extent of carboxylic acid ionization was calculated from the ratio of peak intensity at 1543 cm$^{-1}$ (-COO$^-$ asymmetric stretching) to the sum of the peak intensity at 1543 and 1710 cm$^{-1}$ (-COOH). Here, we assume the coefficient of extinction is the same for the protonated carboxyl at 1710 cm$^{-1}$ and the deprotonated carboxyl at 1543 cm$^{-1}$.\textsuperscript{1-3}

**FTIR-ATR Spectra of Film Surface after Each Process**
Figure S4: FTIR-ATR spectra of the film after each step in the process: the as-assembled BPEI-PAA film, the film after post-assembly acid treatment, crosslinking treatment, silica deposition, chemical vapor deposition, and finally lubricant coating.

Figure S4 shows the FTIR-ATR spectra of the film’s surface after each step in the process. As-prepared BPEI-PAA films have a peak for protonated carboxyl group (-COOH) at 1710 cm$^{-1}$ and deprotonated carboxyl group (–COO$^-$) at 1541 cm$^{-1}$. Peaks at 1610 cm$^{-1}$ (2NH$^+$) and 1645 cm$^{-1}$ (-NH deformation vibration) overlap with the deprotonated carboxylic group. After post-assembly exposure to acid, the ratio of magnitude of the peak for deprotonated carboxylic acid to protonated carboxylic acid groups decrease a little bit, representing the decrease in degree of ionization of the carboxylic acid group in PAA.

Thermal crosslinking is a simple condensation reaction between BPEI and PAA to form amide linkages that also generates water as a byproduct. After thermal crosslinking, the increase in peak intensity at 1645 cm$^{-1}$ is associated with the formation of amide linkages (-CONH-), indicating
the successful chemical linkage between BPEI and PAA. Neither the silica nanoparticle deposition nor the chemical vapor deposition changes the FTIR spectra meaningfully, due to the small amounts of material being deposited during both of those processes. However, the large changes in contact angle values after these steps confirm that deposition is successful at each of these steps.

The multiple peaks, ranging from 1050 to 1400 cm\(^{-1}\) are the asymmetric and symmetric C-F stretches, shown after lubricant coating. The sharp peak at 984 cm\(^{-1}\) comes from C-O stretch. All these high intensity peaks are originated from PEFE.

**Temperature robustness and curved surface coating of polyelectrolyte SLIPS**

![Figure S5](image.png)

**Figure S5.** Temperature robustness and curved surface coating of polyelectrolyte SLIPS. (A) Dynamic contact angle of water and decane droplets with different temperatures on polyelectrolyte SLIPS. The advancing (black) and receding angle (red) of water (square) and n-decane (circle) was taken using a drop volume of 5 µL; (B) Water and oil repellant properties of polyelectrolyte SLIPS coated tube compared with a bare glass tube. The upper phase decane colored with red silicone oil, while the lower phase is water dyed with methylene blue; (C) Water and oil repellant properties of polyelectrolyte SLIPS coated tube compared with a bare
glass tube. The upper phase is methylene blue dyed water while the lower phase is chloroform. The polyelectrolyte SLIPS coated tube has good repellency to both water and oil, however the bare glass tube does not. Movies demonstrating this can be shown in movies S3-S4.

The robustness of the polyelectrolyte SLIPS films via temperature from 25 to 95°C for water and oil was shown in figure S5 (A). Each droplet of specific temperature was transferred to the surface for 30 s before the test, and all of the test points were taken within a 2 cm square sample of the same film. The advancing and receding angles are not significantly different from one another for both cases, and contact angle hysteresis remains small (~2°) over this temperature range.

The polyelectrolyte SLIPS was coated on the curved surface, a glass tube, shown here in Figure S5(B and C). Figure S5(B) shows water dyed with methylene blue (the lower phase) and a mixture of decane with silicone oil (the oil added for color) as the upper phase in the beaker. Figure S5(C) has oil and water phases inverted, and the heavy oil phase used is chloroform. The polyelectrolyte SLIPS on the glass tube can repel water, decane and chloroform without any droplets adhering to the tube’s surface, while the bare glass tube itself will become coated with an adhesion layer, especially the blue dyed water. This can be better visualized by watching movies S3 and S4.

**Pore Size and Distribution after Staged Acid Etching**

**Table S1**: Pore sizes and standard deviations of large microsize pore and small nanosize pores created in the various parts of the staged acid etching. Microscale pores are formed during the first stage of the etching, then the nanopores.
Table S1 shows the average pore sizes (including standard deviation) of 100 large microsize pores and 100 small nanosize pores based on low magnification and high magnification (inserted) SEM images shown in Figure 2.

**Supplementary Movies Legends**

Movie S1 demonstrates the water repellency of polyelectrolyte-based SLIPS. The water droplet (5 µL) slides on a SLIPS at a low tilting angle ($\alpha$=3°) with a contact angle hysteresis lower than 2°. The droplet can move off the screen which is 5 mm in width within a few seconds.

Movie S2 demonstrates the oil repellency of polyelectrolyte-based SLIPS. The decane droplet (5 µL) slides on a SLIPS at a low tilting angle ($\alpha$=3°) with a contact angle hysteresis lower than 2°. The droplet can move off the screen which is 5 mm in width within a few seconds.

Movie 3 demonstrates water and oil repellant properties of polyelectrolyte SLIPS coated tube compared with a bare glass tube. The upper phase decane colored with red silicone oil, while the
lower phase is water dyed with methylene blue. The polyelectrolyte SLIPS coated tube has good repellency to both water and oil, however the bare glass tube does not.

Movie 4 demonstrates water and oil repellant properties of polyelectrolyte SLIPS coated tube compared with a bare glass tube. The upper phase is methylene blue dyed water, while the lower heavy oil phase is chloroform. The polyelectrolyte SLIPS coated tube has good repellency to both water and oil, however the bare glass tube does not.

Movie 5 demonstrates slippery properties of water droplets after chilled to -10°C. The polyelectrolyte SLIPS have been chilled to -10°C for 30 min in the refrigerator, and then set into atmospheric condition in the lab (22°C and 55% humidity). While still cold and condensation having been allowed to form on the surface, the film is shown to still be slippery to water droplets.

Movie 6 demonstrates self-cleaning properties of polyelectrolyte SLIPS. The silica powder was sprinkled on both the polyelectrolyte SLIPS and superhydrophobic polyelectrolyte film without lubricant infusion. The water droplets can roll the silica powder off the film from the SLIPS taking the advantage of the low sliding angle slippery properties.

Reference

