Surface Chemistry

Hydrophobic and Ultrahydrophobic Multilayer Thin Films from Perfluorinated Polyelectrolytes**

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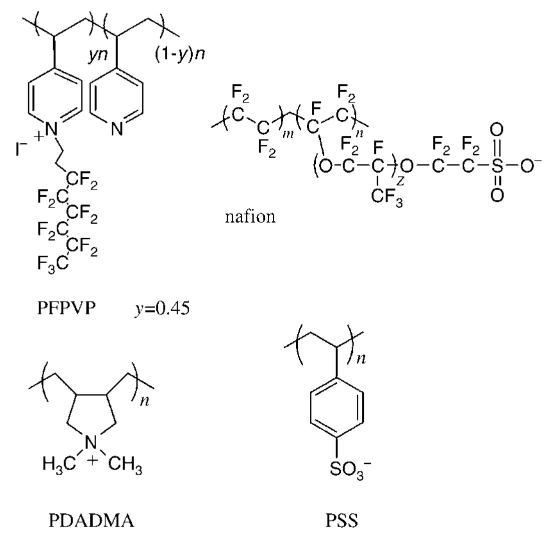
Interest in surfaces exhibiting large water contact angles is stimulated both by important technological implications and by novel aspects of surface physics. Since wetting can be controlled by a single monolayer of material, novel materials or surface treatments can yield a fascinating range of properties. Such treatments, which are capable of generating particularly hydrophobic surfaces, include conventional coating processes such as spraying or dipping,[1a] vacuum deposition techniques,[1b] and such surface-modification technologies as diffusion,[1c] laser and plasma processes,[1d] chemical plating,[1e] grafting[1f] or bonding hydrogel encapsulation,[1g] and bombardment with high-energy particles.[1h]

The use of the layer-by-layer sequential adsorption[2] method for the assembly of an ultrathin film has very recently been reported for making ultrahydrophobic surfaces.[3,4] These studies address the critical issue of inducing surface roughness, which is required for true ultrahydrophobic behavior.[5–15] Soeno et al.[3] described a multilayered polyelectrolyte/silica nanoparticle system which was heated to sinter the particles and burn off the polymer, then treated with a fluorosilane to induce the required hydrophobicity. Zhai et al.[4] reported the formation of a pH-sensitive multilayer which undergoes a porosity-inducing phase transition in acidic solutions. Additional treatment steps, including cross-linking, deposition of silica nanoparticles, fluorosilane treatment, and thermal annealing, yielded stable ultrahydrophobic materials. Although the targeted surface properties were obtained, multiple processing steps are not desirable. Herein, we describe a multilayering process that uses both fluorinated polyanions and polycations, with a roughening step, by utilizing a naturally occurring nanorod that can be inserted conveniently into the layering sequence.

The polyelectrolytes used were nafion (Scheme 1), which is a commercially available sulfonated fluorinated material, and a polycation synthesized from poly(vinylpyridine) and a fluorinated alkyl iodide. Polyelectrolyte components were deposited on silicon wafers under ambient conditions using dilute solutions/dispersions. Although fluorinated solvents, such as trifluoroethanol, were useful for dispersing the polyelectrolytes, we were interested in employing more common solvents as vehicles for manipulating all the components. Methanol was effective in this respect. Figure 1 shows the layer-by-layer build-up of the fluorinated polyelectrolytes. The regular growth of the multilayer alleviated our concerns that the polyelectrolytes, probably existing as micellar, nanoparticulate dispersions rather than true solutions, might not produce acceptable multilayering behavior. Some curvature of the build-up curve hints at exponential growth (a topic of recent interest[16,17]), but the fact that such curvature is so slight suggests it might result from increasing surface roughness, which was found to be 2.9, 3.2, 4.8, 5.7, 7.0, and 10 nm root-mean-square (RMS) for 10, 20, 30, 40, 50, and 60 layers, respectively.



Scheme 1. Structures of the polyelectrolytes.

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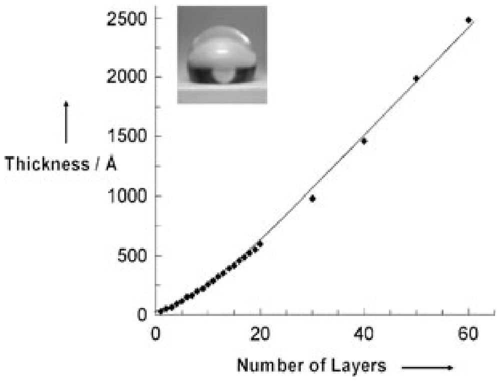

Figure 1. Layer-by-layer build-up of nafion/PFPVP on polished Si(100). The refractive index was measured to be 1.40. The insert shows a droplet of water on the final multilayer.

The contact angles on the fluorinated multilayers, as well as some more common multilayer systems, are summarized in Table 1. Two techniques for measuring the contact angle were employed. The "sessile drop" method involves the use of a telescope (Rame–Hart Inc.) to manually estimate the angle made by a 10-µL drop dispensed on the surface. This method gives a value akin to an advancing contact angle θ_a. Rectangular pieces of a completely coated silicon wafer were also employed to determine the dynamic contact angles (DCA) by using the Wilhelmy plate method.[18] In this method a plate is dipped slowly into water and then withdrawn. After correction for buoyancy, the respective advancing and receding θ_r angles are calculated, which are subject to less operator interpretation than the sessile drop instrument.[19] While the fluorinated surfaces give large advancing contact angles (some larger than for teflon), the value of θ_r is much smaller for smooth hydrophobic surfaces than ultrahydrophobic (rough and hydrophobic) surfaces (Table 1).

Table 1: Water contact angles, both static and dynamic, on various multilayer surfaces.

System	Dynamic contact angle [°]		Static contact angle [°]
	advancing	receding	
blank	21	19	0
$(PDADMA/PSS)_{10}PSS$	41	19	15
$(PDADMA/PSS)_{11}PDADMA$	57	23	35
$PEI(PFPVP/nafion)_{10}PFPVP$	114	28	114
$PEI(PFPVP/nafion)_{11}nafion$	102	37	104
$PDAMA(PSS/PDADMA)_3$-$(clay/PDADMA)_3$ $(nafion/PFPVP)_4PFPVP$	156, 154[a]	143, 142[a]	168, 168[a]

[a] Value measured after 2 months of immersion in water.

Measurements of both θ_a and θ_r, in particular the difference (or hysteresis) between them, are essential for verifying true ultrahydrophobic behavior.[20–22] In the wetting state described by Wenzel,[23,24] a water droplet penetrates the roughness features of the surface and becomes pinned to the surface. Although such a surface might exhibit a large θ_a value, that of θ_r is usually much smaller. By contrast, Cassie and Baxter[25,26] considered a water droplet that rides over the uppermost features of a hydrophobic surface, essentially remaining in contact with air. This surface may exhibit very small contact angle hysteresis, with the result that water droplets roll easily. In a recent critical evaluation of the "superhydrophobic" or "ultrahydrophobic" surface literature, Chen et al. provide numerous examples of systems that are poorly defined because they fail to clearly present contact angle hysteresis.[14] Even very recent work falls short in this respect.[27] Following the recommendation of Chen et al.,[14] we reserve the term "ultrahydrophobic" for those surfaces exhibiting both large water contact angles and small hysteresis between θ_a and θ_r.

It is interesting to note that extremely large contact angles and surface roughness are not prerequisites for ultralyophobicity in non-aqueous liquids (exhibiting "lyophobic" behavior).[14] Ultrahydrophobicity, however, appears to require surface roughness, although the length scales are not well understood. Regularly patterned pillars, produced by lithography, with diameters of approximately 10 µm and about the same spacing generated ultrahydrophobic surfaces.[20,22] In contrast, Zhai et al.[4] focused on reproducing the "lotus effect,"[28] whereby micrometer-sized surface features are decorated with nanometer-sized wax particles. Similarly, we sought to create surface roughening on two length scales—micrometer and nanometer—but using particles inserted as layers in the multilayering process.

Clay minerals constitute one of the many different types of particles that have been employed in the layer-by-layer assembly process.[29] However, most clays are platelike and have been shown to deposit parallel to the substrate during multilayering, thus leading occasionally to short-range order. Such tiling would not be optimum for surface roughness. For this purpose we employed attapulgite, a clay mineral with an unusual needlelike morphology.[30] Attapulgite (also known as Palygorskite or Fuller's Earth) is magnesium aluminum silicate clay of very fine particle size.[31,32] The average particle length is between 1 to 2 µm, with widths from 10 to 50 nm. As such, attapulgite represents an intriguing, naturally occurring nanorod. By using the multilayering design (the detailed sequence is summarized in Table 1) we deposited three strata. The first, adjacent to the substrate, consisted of a few layer pairs of poly(diallyldimethylammonium)/poly(4-styrenesulfonate) (PDADMA/PSS) deposited from a 0.8 M salt solution. This served as an initial "bed" for the particles. The next stratum alternated clay particles (which bear a negative surface charge) with PDADMA to produce roughness. The final stratum comprised the fluorinated polyelectrolytes. The entire process was performed under ambient conditions in common solvents. No annealing steps were required.

This tri-strata approach (one of many similar variations) produced ultrahydrophobic surfaces, as indicated by a small hysteresis between θ_a and θ_r (Table 1). Several experimental refinements were needed. Optimally, the clay nanorods must protrude from the surface so that droplets are able to ride over them in a manner similar to that reported by Cassie and Baxter. This arrangement is contrary to the expected fate of individual objects of high aspect ratio, which would tend to lie flat on the surface. Thus, sonicating a dispersion of the clay in water for 24 h proved counterproductive. There is also the possibility that the clay nanorods would bundle together along their long axes instead of forming “spiky” aggregates. The attapulgite dispersion appears to have cooperated in this respect, as seen in Figure 2, which shows aggregates on the micrometer scale of disordered clay particles of nanometer dimensions. The separation between the larger aggregates is also on the order of a few micrometers. It is not possible to discern from the micrographs whether the polyelectrolytes deposit as a continuous coating on the particles, but hydrophobic material is clearly sufficiently well dispersed to make the surface homogeneously ultrahydrophobic. Heterogeneity was more of a problem from the roughening perspective: for example, if salt was added to the PDADMA solution used to generate the PDADMA/clay stratum, the density of the agglomerates on the surface was lower (as seen by SEM and also the surface appears less hazy to the eye). Water exhibited a large contact angle to the surface coated with the fluorinated stratum, but only localized areas gave a small contact angle hysteresis, and the DCA traces were very ragged, thus indicating multiple pinnings of the receding water front. A multilayer nanocomposite (Figure 2) with uniform (over the whole 2.5-cm diameter wafer) ultrahydrophobic behavior and a surface rms roughness of 3.2 μm was obtained with salt present in the clay suspensions and no salt in the PDADMA for the PDADMA/clay stratum.

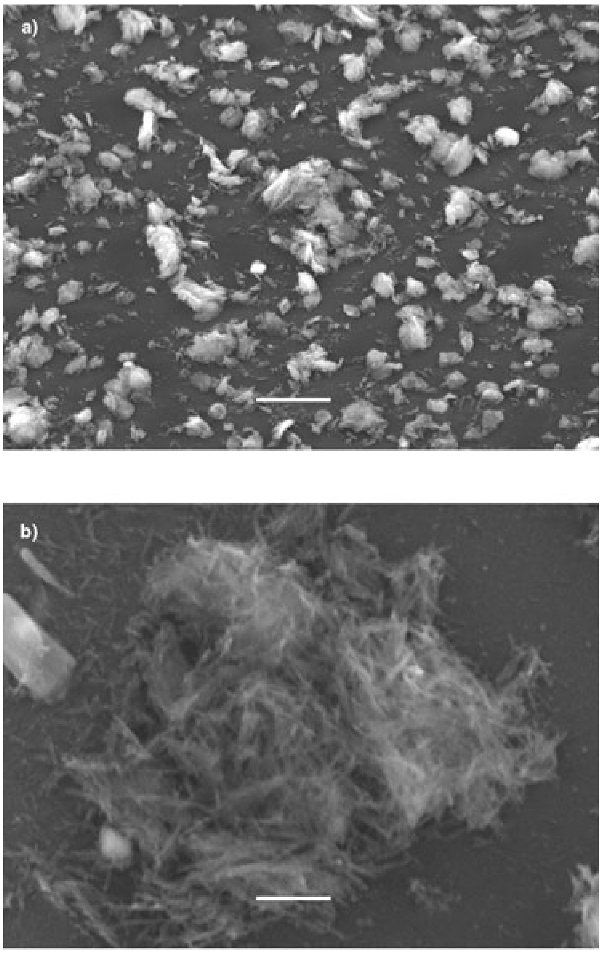

Figure 2. Scanning electron micrographs of the polyelectrolyte–clay ultrahydrophobic multilayer (PSS/PDADMA)$_3$(clay/PDADMA)$_3$-nafion/PFPVP)$_4$PFPVP. a) Scale bar = 20 μm and b) scale bar = 2 μm scale. The SEM stage was tilted 50°.

Immobile droplets (Figure 3) were very hard to obtain. Attempts were made to level the substrate, but a slope of only a degree or so exceeded the critical angle for rolling.[33] In fact, we believe that the droplet shown in Figure 3 has been loosely pinned by a defect. This surface remained ultrahydrophobic after being immersed in water for more than two months—neither static nor dynamic contact angles changed over this time period (Table 1). The thermal stability of the multilayer from Figure 2 was assessed by heating it at 120 °C for 24 h in air. There were no changes in the contact angles.

Figure 3. Water drop on the surface of the ultrahydrophobic multilayer surface from Figure 2. The diameter of the drop is about 2 mm.

The contact angle is exquisitely dependent on the hydrophilicity of the top layer. The ultrahydrophobic film from Figure 2 was transformed into an ultrahydrophilic surface by coating it with 2.5 additional layer pairs of a 1 mM solution of PAA-*co*-PAEDAPS/PFPVP (that is, with (PAA-*co*-PAEDAPS/PFPVP)$_2$PAA-*co*-PAEDAPS; PAA-*co*-PAEDAPS is a statistical copolymer of 75 mol % poly(acrylic acid) and 25 mol % poly((3-[2-(acrylamido)-ethyldimethylammonio]-propane sulfonate), a zwitterion).[34] It is very hydrophilic. The rough multilayer terminated with this polymer had a contact angle of 0° (too small to measure).

In conclusion, we have demonstrated a facile method of generating ultrahydrophobic surfaces from a novel combination of fluorinated polyelectrolytes and natural nanorods. Several issues remain to be addressed. Of interest is the critical spacing between roughness features that characterizes a transition between a pinning (Wenzel) and a free-rolling (Cassie–Baxter) ultrahydrophobic surface. Any characteristic distances will be averages, as the deposition of nanorod agglomerates is random.

Experimental Section

Poly(4-vinylpyridine) (M_W 300000) was alkylated to a level of 45 ± 3% with 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodooctane (TDFI, $C_8H_4F_{13}I$) to give the fluorinated polycation PFPVP by using a 1:1 (v/v) mixture of DMF and nitromethane. Multilayers were prepared from this and nafion (Aldrich) using 1 mM solutions of the polyelectrolyte (based on the repeat unit) in methanol. The polished Si(100) wafers were exposed to polyelectrolyte solutions for 10 min with stirring, with 3 intermediate rinses in methanol for 30 s. Some substrates were primed with one layer of polyethyleneimine (PEI). The clay solution consisted of 0.2 wt% attapulgite (Attagel 50, Englehard Inc.) in distilled water. The immersion time for each clay layer was 1 h, followed by 3 rinses in distilled water.

The thickness of the film was measured with an ellipsometer (Gaertner L116S) or a profilometer (KLA Tencor P15). The profilometer was also used for measuring the rms surface roughness and thickness of the ultrahydrophobic film. Atomic force microscopy (Dimension 3100, Digital Instruments) was used to determine the surface roughness of the nafion/PFPVP films. The contact angle was measured by the sessile drop method (Rame-Hart telescope) or by a dynamic contact angle instrument (Cahn Instruments). Care was taken to coat the rectangular Si wafer substrates for DCA uniformly. The following shorthand for multilayers is used: $(A/B)_x$ where A is the starting cationic polyelectrolyte contacting the substrate, B is the anionic polyelectrolyte, and x is the number of layer pairs. In $(A/B)_xA$, A would be the terminating polymer. The salt MY (cation M^+ and anion Y^-) plays an important role in the build-up process and is represented by $(A/B)_x@c$MY, where c is the molarity of the salt (MY) in the polymer solution.

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