Supporting Information

Surface-Initiated Polymerization of Superhydrophobic Polymethylene

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Experimental Methods

Materials. Ethanol (ACS/USP grade) was used as received from AAPER. Thiolacetic acid (98%) and 1,2,4 trichlorobenzene (99%) were obtained from Acros Organics. Sodium hydroxide (ACS grade), potassium hydroxide (ACS grade), hexane (HPLC grade), hydrochloric acid (36.5-38%), and concentrated sulfuric acid (95-98%) were used as received from EMD Chemicals. 5-Hexenyltrichlorosilane was purchased from Gelest Inc. and used as received. Acetone (ACS grade), benzoic acid (ACS grade), ethyl acetate (HPLC grade), methanol (HPLC grade), toluene (ACS grade), hydrogen peroxide (30%, ACS grade), and chromatographic silica gel (60-100 mesh) were used as received from Fisher Scientific. Sodium methoxide (>97%) was obtained from Fluka. Nitrogen, and oxygen were obtained from J&M Cylinder Gas Inc., and Airgas, Inc., respectively. 11-Bromo-1-
undecene (95%), 1-octene (98%), borane-tetrahydrofuran (THF) complex solution (1.0 M), Diazald (N-methyl-N-nitroso-P-toluenesulfonamide, 99%), anhydrous diethyl ether (>99%), phenolphthalein (ACS grade), silver sulfate (99.999%), and anhydrous tetrahydrofuran (>99.9%) were acquired from Sigma-Aldrich. Deionized water (16.7 MΩ•cm) was purified using a Modu-Pure system and used for electrochemical characterizations and rinsing. Gold shot (99.99%) and chromium-coated tungsten filaments were purchased from J&J Materials and R. D. Mathis, respectively. Silicon wafers (100) were obtained from Montco Silicon, rinsed with water and ethanol, and dried in a stream of nitrogen. Polished gold-coated QCM quartz crystals (5 MHz) were obtained from Inficon and precleaned in piranha solution (7:3 H$_2$SO$_4$:H$_2$O$_2$(aq) in volume) before use.

**Preparation of Diazomethane.** DM was carefully synthesized according to literature to produce a c.a 16 mM solution in diethyl ether.$^1$ According to each experiment, the original DM solution was diluted in ether to the targeted concentration and stored at -17°C. The concentration of DM was determined by titration with benzoic acid.$^1$ Caution: Diazomethane is toxic and potentially explosive, and should be handled carefully.$^1$

**Synthesis of Undec-10-ene-1-thiol.** The thiol was synthesized from the corresponding bromide by sequentially using the thioacetate method$^2$ and acidic solvolysis conditions.$^3$ Under a nitrogen atmosphere 11-bromo-1-undecene (1.543 g) and thiolacetic acid (0.529 g) were added to 61 mL of methanol in a stirred flask. The system reacted for 10 h under reflux, and thin film chromatography (TLC) using hexane as solvent was used to determine the end of the reaction. After the bromide completely reacted, hydrochloric acid was added to the system under N$_2$ atmosphere and reacted for 12 h. Depletion of the acetate was determined by TLC using a solution of hexane/ethyl acetate (30/1) as solvent. At the end of the reaction, the product was dissolved in hexane, washed with water and dried by addition of calcium chloride, followed by decantation of the organic phase. To purify the thiol, the organic phase was concentrated using vacuum distillation and then separated using column chromatography with a solution of hexane/ethyl acetate (30/1). Finally, the thiol was concentrated using a rotovapor.
**Preparation of Gold- and Silver-modified Gold Substrates.** Silicon (100) wafers were rinsed with water and ethanol and dried in a stream on N2 prior to placing in a metal atom evaporator and reducing the pressure to $4 \times 10^{-6}$ Torr with a diffusion pump. Then, chromium (100 Å) and gold (1250 Å) were evaporated in sequence onto silicon at rates of 1-2 Å s$^{-1}$. After bringing the chamber to atmospheric pressure and removing the gold-coated silicon wafers, 1.2 cm x 4 cm gold samples were cut from the wafer, rinsed with ethanol, and dried with N2 before use.

Silver-modified gold (Ag/Au) substrates with a fractional coverage of 0.9 (90%)$^4$ were prepared by electrochemically cycling 1.2 cm x 4 cm gold-coated silicon samples (working electrodes) in a 0.1 M H$_2$SO$_4$(aq) solution containing 0.6 mM Ag$_2$SO$_4$, using a CMS300 potentiostat (Gamry Instruments) connected to a personal computer. The working electrode was emersed under a controlled potential on the cathodic scan at 60 mV. Upon emersion from the electrochemical cell, the UPD-modified substrates were rinsed with water and ethanol, dried with nitrogen, and quickly exposed to conditions for SAM formation.

Vinyl-terminated self assembled monolayers (SAM) on Au and Ag/Au substrates were prepared by immersing the samples for 12 h in a 1 mM undec-10-ene-1-thiol solution in ethanol. After removal from the thiol solution, the samples were rinsed with ethanol and dried with nitrogen.

**Preparation of Silicon Substrates.** Silicon (Si) substrates were cut from silicon wafers into 1.2 cm x 4 cm samples, sonicated in ethanol for 30 min, and dried in a stream of nitrogen. Then, the samples were exposed to piranha solution (14 mL H$_2$SO$_4$: 6 mL H$_2$O$_2$) for 45 min to remove adventitious carbon and generate a hydroxylated surface. The samples were rinsed 4 times by submersion in water and once in ethanol and dried thoroughly in a stream of N$_2$. Monolayers were formed on silicon surfaces by immersing the samples in a 1 mM solution of 5-hexenyltrichlorosilane solution in anhydrous toluene for 5 h. Upon removal from solution, the samples were rinsed in toluene and dried in a stream of N$_2$.

**Preparation of Polymer Films.** Vinyl-terminated monolayers on Au, Ag/Au, and Si were placed under nitrogen in a septum-capped vial by 3 cycles of evacuation followed by N$_2$ backfilling. A 0.1 M solution of borane in THF was added to the vial via cannula. After 2 h of reaction, the borane solution
was evacuated from the system and the samples were rinsed 3 times with anhydrous THF via cannula. Finally, the samples were immersed in a DM solution at -17 °C for various times, and upon removal from the DM solution, they were vigorously rinsed with trichlorobenzene and ethanol, and dried in a stream of nitrogen.

**Oxidation of Hydroborated Films.** Hydroborated monolayers on Au and Ag/Au were preoxidized by exposing freshly prepared monolayers to O$_2$-saturated THF for 1 h and water for 30 min (HBO), followed by rinsing the monolayers with ethanol and water and drying them with a stream of nitrogen. Hydroborated monolayers on Si were oxidized by exposing the surfaces to a 0.2 N solution of NaOH in H$_2$O$_2$ (30%). The system reacted for 12 h under inert atmosphere, and the resulting monolayers were rinsed with ethanol and water, and dried under a stream of nitrogen.

**Characterization Methods.** Thicknesses of films grown from non-hydroborated surfaces were measured with a J.A. Woollam XLS-100 variable angle spectroscopic ellipsometer. At a 75° angle of incidence, 100 revolutions/measurement were taken across a range of wavelength (200-1000 nm) for each sample. WVASE 32 Version 3.374 software was used to model and calculate the thickness of the films. For films on Au and Ag/Au, fresh and uncoated substrates served as a baseline for thickness measurements and were used to determine the optical constants of the substrate. The film thickness was estimated as the average of three measurements at different points across the substrate, using the Cauchy model with the coefficients set at $A = 1.5$ and $B = C = 0$. Reported errors represent the averages and standard deviations, respectively, from at least two independently prepared films.

Thickness measurement of films grown from SIPM were performed using profilometry and quartz crystal microgravimetry (QCM). Profilometry measurements were performed in a Veeco Dektak 150 profiler, using 49 μN of force and the hills and valleys detection mode. Thickness was estimated by scratching the surface, scanning 500-1000 μm across the scratch and plane-fitting the scan results using the instrument software. Reported errors represent the averages and standard deviations of at least two independently prepared films.
QCM measurements were performed with a PM-700 series plating monitor (Maxtek, Inc.) to estimate the film thicknesses on polymethylenated surfaces. Polished, gold-coated quartz crystals (5 MHz, Maxtek) were cleaned with piranha solution (7:3 H$_2$SO$_4$:H$_2$O$_2$(aq) by volume) before use. Ag-modified gold crystals were prepared by upd as described above. Upon emersion from the electrochemical cell, the Ag/Au crystal was rinsed with water and ethanol, dried with N$_2$, and quickly mounted in the QCM probe. After determining the QCM reference frequency, the crystal was removed from the probe and was then immediately immersed into thiol solution and subsequently polymerized as described above. The change in the characteristic resonant frequency (Δf) of the crystal was determined after polymerization, and from this value, the change in mass (Δm) was calculated using Sauerbrey’s equation:\(^9\)

\[ \Delta m = -\frac{A\left(\rho_q \mu_q \right)^{1/2} \Delta f}{2f_0^2} \]  

(6)

where \( f_0 \) is the original crystal oscillation frequency (5 MHz), \( A \) is the surface area of the crystal gold electrode (1.327 cm$^2$), and \( \rho_q \) and \( \mu_q \) are the crystal density (2,648 kg/m$^3$) and the crystal elastic shear modulus (2.947x10$^{10}$ kg m$^{-1}$ s$^{-2}$),\(^{10}\) respectively. The average thickness of the PM films can be estimated by dividing \( \Delta m \) with \( A \) and \( \rho \), where \( \rho \) is the film density, assumed to be the same as that of bulk PM (0.92 g/cm$^3$).\(^{11}\)

PM-IRRAS spectra for SAMs were collected using a Brucker PMA-50 attachment to a Bruker Tensor 26 infrared spectrometer equipped with a liquid-nitrogen cooled mercury-cadmium-telluride (MCT) detector and a Hinds Instruments PEM-90 photoelastic modulator. The source beam used a half-wavelength (λ/2) retardation modulated at a frequency of 50 kHz and set at 80° incident to the sample surface. Spectra for SAMs on gold substrates were collected over 5 min (380 scans) at a resolution of 4 cm$^{-1}$.

RAIR spectra for PM films on Au and Ag/Au substrates were collected with a Varian Excalibur FTS-3000 infrared spectrometer using p-polarized light incident 80° from the surface normal. The
instrument was run in single reflection mode using a universal sampling accessory and a nitrogen-cooled, narrow-band MCT detector. A background spectrum was collected on Au and Ag/Au previously exposed to deuterated \( n \)-dodecanethiol (\( \text{C}_{12}\text{D}_{25}\text{SH} \)). After the reference sample was exposed to ambient air, a second spectrum was collected to be subtracted from the spectrum of all films to eliminate peaks due to ambient humidity. Each spectrum was collected over 200 scans with a spectral resolution of 2 cm\(^{-1}\).

The XPS analysis was performed using a PHI 5000 VersaProbe spectrometer. Samples were irradiated with a 25 W monochromatic Al K\( \alpha \) X-ray (1486.7 eV) with a 100 \( \mu \)m spot size. Photoelectrons were collected from a 45° takeoff angle with respect to the surface normal into a spherical capacitor analyzer operated in constant pass energy mode. Both an electron neutralizer of 1.1 eV and an \( \text{Ar}^+ \) ion neutralizer of 10 eV were used on all samples to counteract any charging effects. Survey spectra were collected over a binding energy range from 0-1300 eV at a pass energy of 187.7 eV. High resolution spectra were collected at a pass energy of 58.7 eV. All spectra were collected over a 400 by 400 \( \mu \)m area. Data were analyzed using CasaXPS data analysis software to calculate the atomic percentages using the peak area and elemental region sensitivity factors.\(^{12}\)

EIS was performed with a Gamry Instruments CMS300 impedance system interfaced to a personal computer. The working electrode was mounted in a Flat Cell (EG&G) in which 1.0 cm\(^2\) of the sample was selectively exposed to an aqueous solution of 1 mM K\(_3\)Fe(CN)\(_6\), 1 mM K\(_4\)Fe(CN)\(_6\)•3H\(_2\)O, and 0.1 M Na\(_2\)SO\(_4\). Measurements were obtained using a Ag/AgCl, saturated KCl electrode as reference and an evaporated gold on silicon substrate as counter electrode. Data were collected between 10\(^{-1}\) and 10\(^4\) Hz.

SEM images were obtained using a Raith e-Line electron beam lithography (EBL) system equipped with a thermal-assisted field emission gun at 10 keV. AFM images were obtained with a JEOL 5200 scanning probe microscope (SPM) under an ambient laboratory environment. Areas of 1.5-10 \( \mu \)m were scanned in tapping mode with a silicon nitride tip, and the images were plane-fitted and filtered to remove noise using the instrument software.
Advancing and receding contact angles were measured with a Rame-Hart goniometer on static ~5 µL drops. A syringe was used to apply DI water, in which the needle of the syringe remained inside the probe fluid droplet as the advancing and receding contact angle measurements were taken. Reported errors represent the averages and standard deviations, respectively, from at least four independently prepared films.

**Phase Angle Plot.** To investigate the effect that trapped air at the polymer/water interface has on the barrier properties against redox probes, we characterized PM films with electrochemical impedance spectroscopy (EIS) in the presence of 1 mM K₃Fe(CN)₆, 1 mM K₄Fe(CN)₆·3H₂O, and 0.1 M Na₂SO₄(aq). Figure S1 shows the variation of the phase angle in the 10⁻¹ to 10⁵ frequency window for the six same substrates in Figure 7. The phase angle plot describes the balance between a pure capacitive (φ = -π/2) and a pure resistive (φ = 0) behavior of the films. In our case, the figure shows that the superhydrophobic film grown from HB+Au displays a purely capacitive behavior with no signs of variation towards a resistive component at low frequencies, whereas the non-superhydrophobic PM film grown from HB+Ag/Au (θₐ/θᵣ=162°/149°) displays a slight increase in φ at low frequencies, consistent with the onset of limited penetration by redox probes. This behavior highlights the role of superhydrophobicity in the ability of the film to perfectly block the redox probes from the substrate.
References