Supporting Information

Porosity Effects on the Ordering and Stability of Self-Assembled Monolayers on Nanoporous Gold

*Dipna A. Patel, Robert B. Chevalier, Andrew M. Weller, Christopher C. Shakespeare, Edward J. Soares, Elizabeth C. Landis**

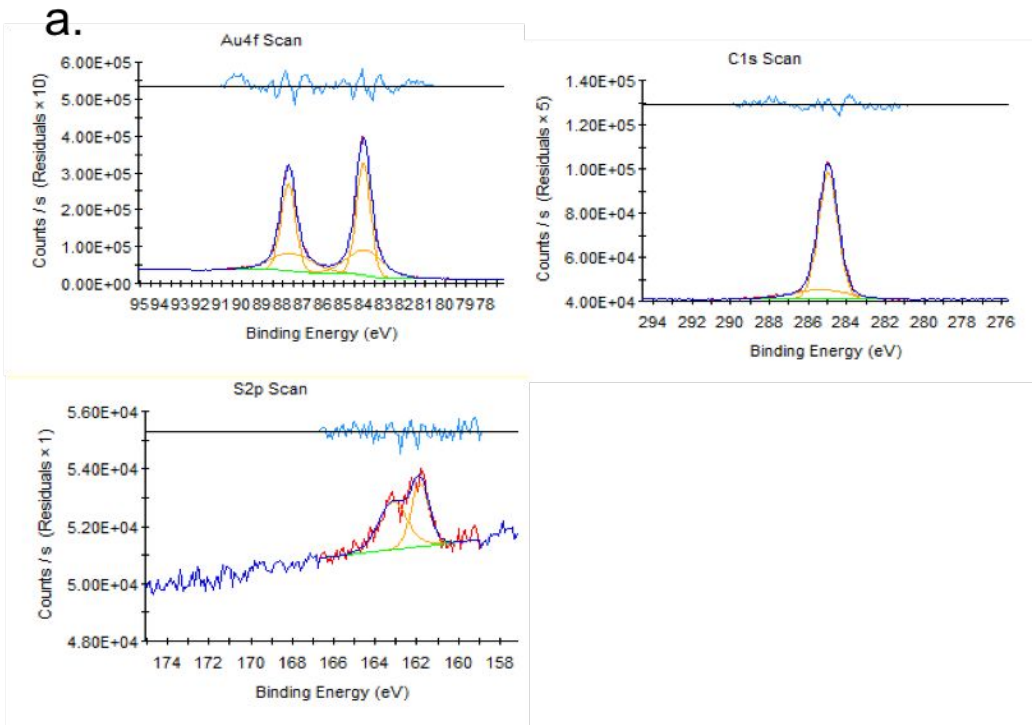
Department of Chemistry, College of the Holy Cross, 1 College St Box C, Worcester, MA 01610

Department of Mathematics and Computer Science, College of the Holy Cross, 1 College St., Worcester, MA 01610

AUTHOR EMAIL ADDRESS: elandis@holycross.edu, (508)793-2662

1. X-ray photoelectron spectroscopy of molecular layers on nanoporous gold

X-ray photoelectron spectroscopy (XPS) was collected on a Thermo Scientific K-Alpha XPS using monochromatic Al K_a X-rays at 1.4866 keV with a 400 µm spot size. All spectra were collected with a flood gun to minimize sample charging. Survey spectra were collected using a 1 eV/step, 10 ms dwell time, and 200 eV pass energy. High-resolution scans were collected using a 0.1 eV/step, 50 ms dwell time, and 50 eV pass energy. Spectra were collected using 10 scans for carbon, 40 scans for iron, 30 scans for sulfur, and 3 scans for gold and were corrected using sensitivity factors. Peaks were fit with the Thermo Advantage program using a Smart background correction. All XPS measurements were collected the day after samples were removed from solution. Control experiments demonstrated that the day in air did not cause a measurable change in the XPS spectra.



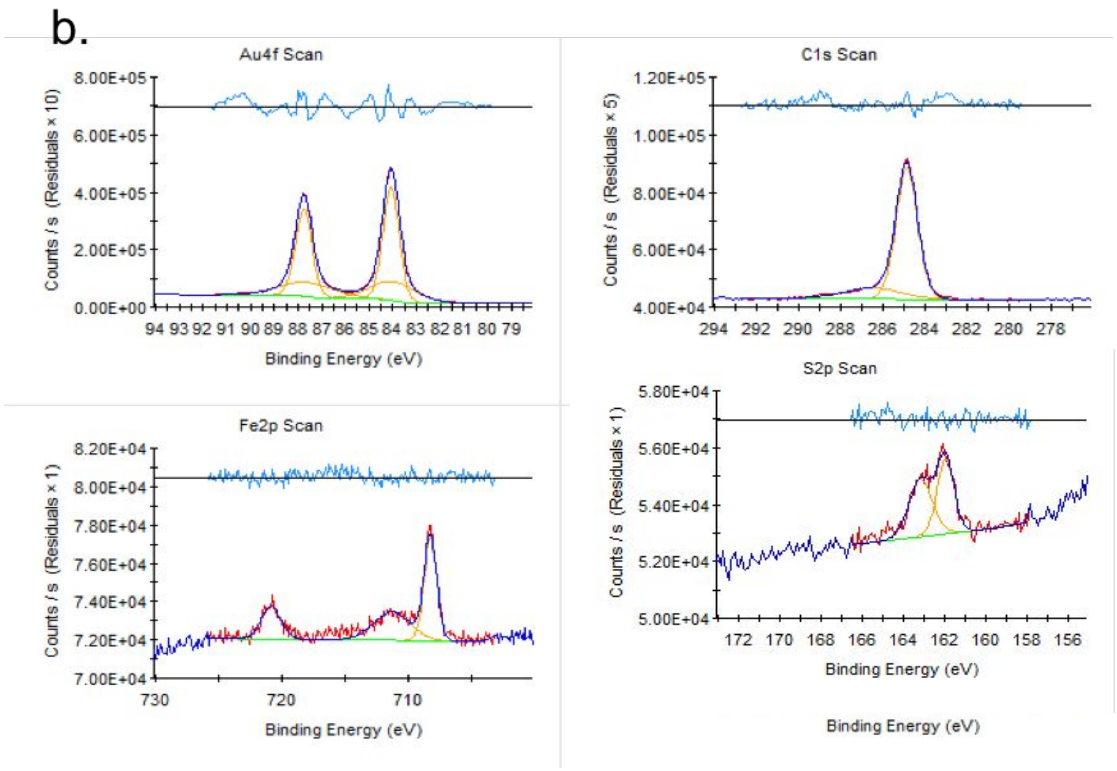


Figure S1. X-Ray photoelectron spectroscopy of nanoporous gold samples functionalized for 7 days in solutions of **a.** 1 mM 1-octadecanethiol, **b.** $\chi_{Fc}^{soln} = 0.40$. Samples were rinsed in ethanol for 30 minutes following functionalization.

2. Pb-UPD data quantification

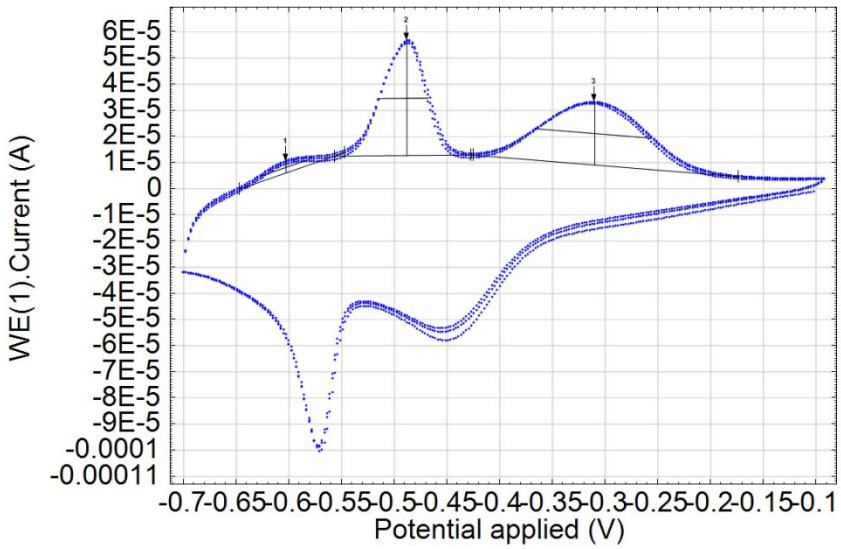


Figure S2. Lead underpotential deposition (Pb-UPD) example quantification, performed using NOVA 1.11 software with a linear curve cursor baseline mode. Peaks were initially detected using the automatic peak search mode. Quantification was performed manually using the second sweep for each cyclic voltammogram.

3. Stability of ferrocene on nanoporous gold

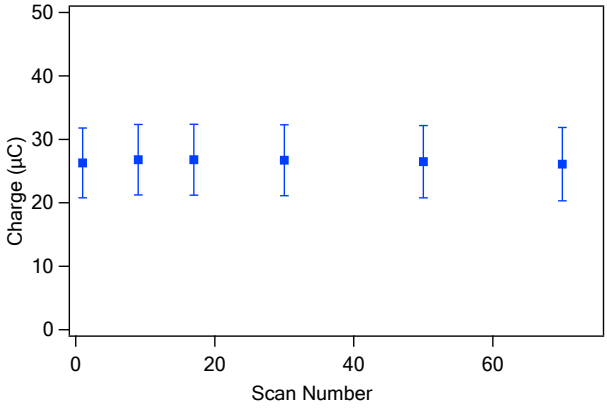


Figure S3. Average oxidation peak area for repeated cyclic voltammograms of $FcC_{11}SH$ on nanoporous gold dealloyed for 24 hours, plotted against the cyclic voltammetry scan number. Cyclic voltammograms were collected at 250 mV/s in 1.00M $NaClO_4$. Peak areas were measured using NOVA 1.11 software.

4. Nanoporous gold surface area measurements

The surface area of nanoporous gold substrates was measured using electrochemical oxidation and reduction of the gold oxide peak. Cyclic voltammograms were collected in a 0.50 M H_2SO_4 solution from 0 to 1.5V at 100 mV/s. Integration of the reduction peak was used to determine the charge required to strip the Au oxide layer, and the conversion factor of 390 μC/cm^2 was used to calculate the surface area.[1]

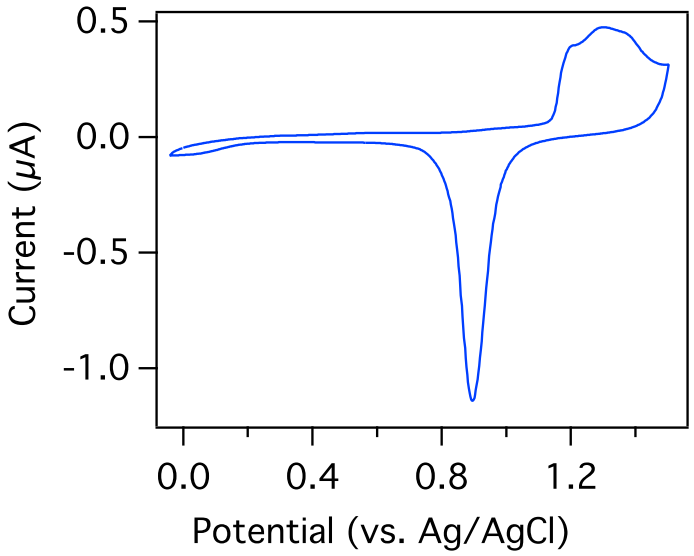


Figure S4. Cyclic voltammogram of gold oxide reduction, collected on nanoporous gold dealloyed for 48 hours in 0.50 M H_2SO_4 at 100 mV/s.

5. Sample cyclic voltammetry curve fits

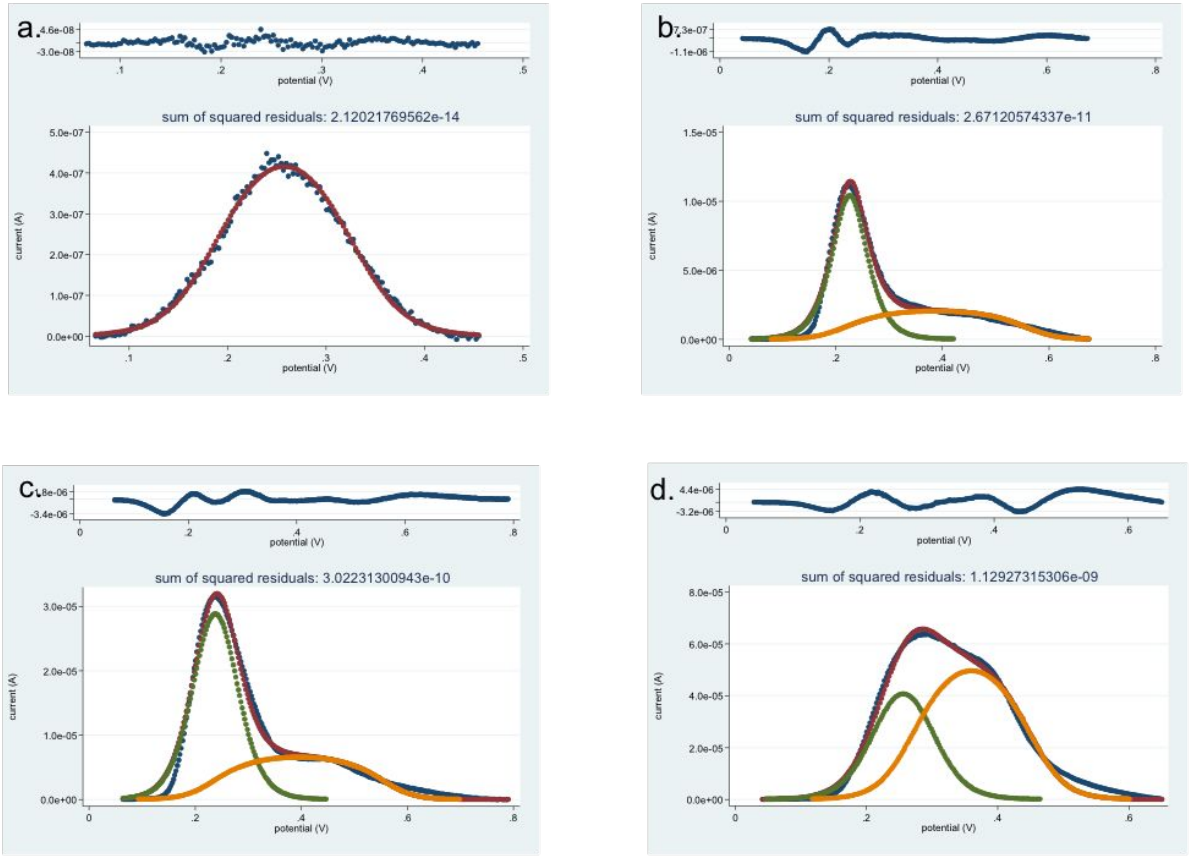


Figure S5. Sample curve fits for nanoporous gold dealloyed for 2 hours and functionalized in mixtures of $FcC_{11}SH$ and $C_{11}SH$ with (a) $\chi_{Fc}^{soln} = 0.10$ (b) $\chi_{Fc}^{soln} = 0.40$ (c) $\chi_{Fc}^{soln} = 0.60$ (d) $\chi_{Fc}^{soln} = 0.80$. Peaks were fit with with Frumkin isotherms following the work of Laviron.[2]

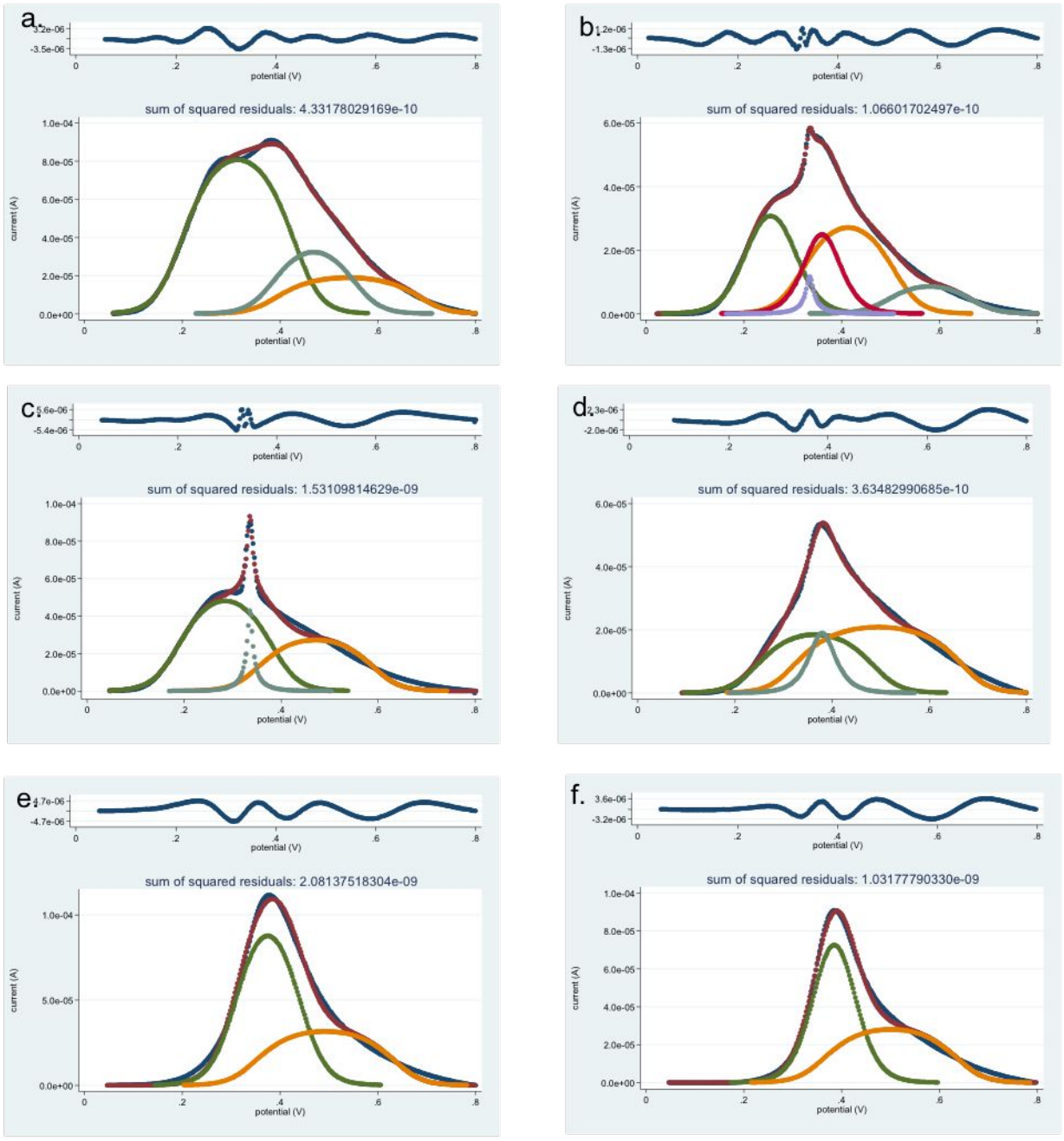


Figure S6 Samples curve fits for nanoporous gold functionalized in 1 mM $FcC_{11}SH$ for 7 days. Nanoporous gold samples were dealloyed for (a) 30 minutes (b) 2 hours (c) 8 hours (d) 12 hours (e) 24 hours (f) 48 hours. Peaks were fit with with Frumkin isotherms following the work of Laviron.[2]

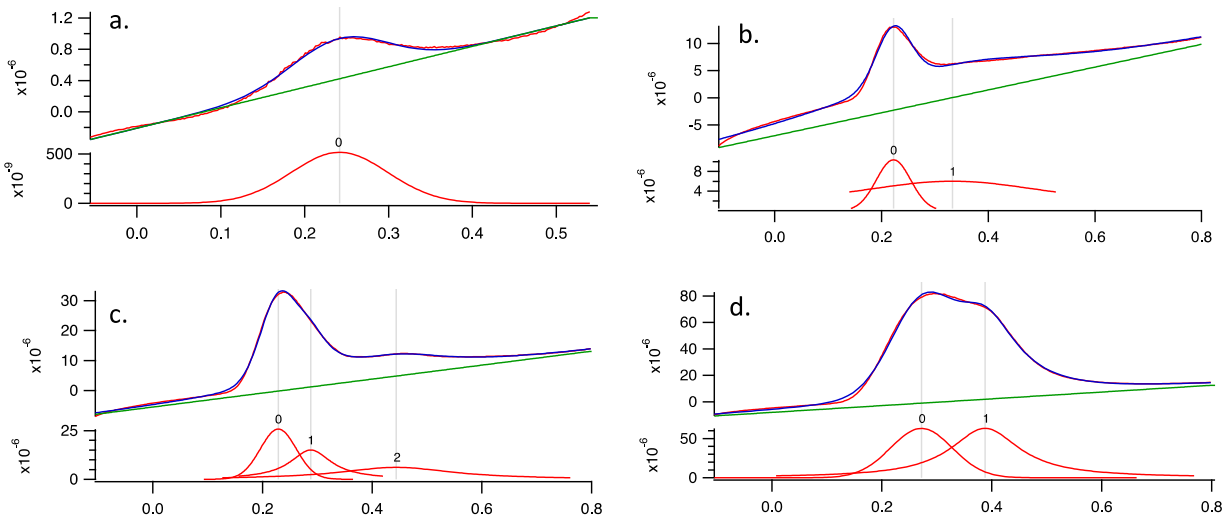


Figure S7. Sample curve fits for nanoporous gold dealloyed for 2 hours and functionalized in mixtures of $FcC_{11}SH$ and $C_{11}SH$ with (a) $\chi_{Fc}^{soln} = 0.10$ (b) $\chi_{Fc}^{soln} = 0.40$ (c) $\chi_{Fc}^{soln} = 0.60$ (d) $\chi_{Fc}^{soln} = 0.80$. Peaks were fit with a combination of Gaussian and Lorentzian functions following the procedure described by Lee et. al. and fits were used to calculate peak areas and ferrocene coverage.[3]

Table S1. Surface density of $FcC_{11}SH$ molecules, reported in moles Fc/cm^2 and calculated for each solution mole fraction of $FcC_{11}SH$ and nanoporous gold dealloying time.

Dealloying time	$\chi_{Fc}^{soln} = 0.1$	$\chi_{Fc}^{soln} = 0.4$	$\chi_{Fc}^{soln} = 0.6$	$\chi_{Fc}^{soln} = 0.8$	$\chi_{Fc}^{soln} = 1.0$
0.5 h	5.1×10^{-13}	4.7×10^{-11}	9.7×10^{-11}	3.6×10^{-10}	5.6×10^{-10}
2 h	9.6×10^{-13}	5.9×10^{-11}	1.0×10^{-10}	3.4×10^{-10}	5.6×10^{-10}
8 h	1.2×10^{-12}	5.7×10^{-11}	1.1×10^{-10}	3.1×10^{-10}	5.2×10^{-10}
48 h	1.3×10^{-12}	6.1×10^{-11}	1.1×10^{-10}	3.5×10^{-10}	5.8×10^{-10}

References

(1) Trasatti, S.; Petrii, O. A. *Pure Appl. Chem.* **1991**, *63* (5), 711–734.
(2) Laviron, E. *Electroanal. Chem. Interfacial Electrochem.* **1974**, *52*, 395–402.
(3) Lee, L. Y. S.; Sutherland, T. C.; Rucareanu, S.; Lennox, R. B. *Langmuir* **2006**, *22* (9), 4438–4444.