Supplemental Information for:

Gold Oxide as a Protecting Group for Regioselective Surface Chemistry

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Experimental Section

General. Hexadecylthiol (92.0%) and Iodine (99.8%) was purchased from Aldrich and used as received. Lithium perchlorate ($LiClO_4$, 99.0%), 1-Iodo-1H,1H,2H,2H-perfluorododecane (97%), and sodium thiosulfate pentahydrate (99%) were used as received from Alfa Aesar. Reagent grade methanol (99.9%) and hexanes (95.8%) were used as purchased from Pharmco-AAPER and Commercial Alcohols. Ethanol (Anhydrous, J.T. Baker, 95%) was used as received. Acetonitrile (ACN, Acros, 99.8%) and tetrahydrofuran (THF, Mallinckrodt, 99%) were purified and dried using a PureSolv system (Innovative Technology, Inc.). Silver nitrate (Fisher, 99.8%) was used as received. Hydrogen peroxide (30%) and sulfuric acid (95%) were used as received from EMD. Hexadecane (99%, Aldrich) was passed through activated alumina twice before use in contact-angle measurements. Gold (99.999%) was used as supplied by VEM Vacuum Engineering. Dihexadecyl disulfide, $[CH_3(CH_2)_{15}S]_2$, was synthesized by the oxidation of hexadecylthiol with iodine.[1]

Preparation of Gold Electrodes. Two gold electrodes were prepared on a single substrate by the application of 5-mm-wide polyimide tape along the center of a piranha-cleaned glass slide prior to metal deposition. Approximately 50 Å of Ti (as an adhesion promoter) and then 1000 Å of Au were evaporated onto the substrates by e-beam vapor deposition. *Caution: Piranha solution, a 4:1 (v/v) mixture of concentrated* H_2SO_4 *and 30%* H_2O_2*, reacts violently with organic material and should be handled carefully.* After metal deposition, the tape was removed to produce two electrically isolated electrodes, ~1 cm wide and separated by a ~5-mm space. Electrodes were used soon after deposition, or cleaned prior to use by adsorption of a SAM from hexadecyl thiol in ethanol (1 mM, 24 h) and subsequently cycling its potential (-1.2 V to 1.5 V, 100 mV/s) ten times in 0.5 M aqueous sulfuric acid to remove any contaminants.

Synthesis of $[CF_3(CF_2)_9(CH_2)_2S]_2$**.** The starting material, $CF_3(CF_2)_9(CH2)_2S_2O_3Na$, was synthesized using a previously published procedure.[2] This compound (0.50 g, 0.73 mmol) was dissolved in 200 mL of ethanol, and I_2 (0.185 g, 0.730 mmol) was dissolved in 50 mL of methanol. The I_2 solution was slowly added to the alkyl-thiosulfate solution with stirring, and the reaction mixture was allowed to stir at room temperature for 48 h. A few drops of 3 M aqueous $NaHSO_3$ were added to reduce the excess I_2. A 50/50 (v/v%) mixture of water and ether was then added to the reaction mixture, and the ether phase was separated. The solvent was removed from this phase by rotary evaporation. The product was then washed with water and analyzed by NMR (yield, 67%).

Contact-Angle and Ellispometry Measurements. Advancing contact angles of water and of hexadecane were measured with a Rame-Hart NRL model 100 goniometer. A minimum of six measurements on three independent drops were made for each sample. Ellispometric parameters (psi and delta) were collected using a J. A. Woollam variable-angle spectroscopic ellipsometer (VASE). Data were collected at angles of 60.00° and 70.00° in the range of 300-800 nm, and thicknesses were calculated with the WVASE32® software using the refractive index of hexadecane over this range of wavelength (measured independently) as a model for the monolayer.

Electrochemistry. Gold oxide was produced electrochemically in 0.5-M sulfuric acid using a standard three-electrode cell comprising a gold working electrode, a platinum wire as the counter-electrode, and an aqueous Ag/$AgNO_3$ (10 mM) reference electrode. To oxidize each electrode, its potential was held at -0.2 V for 10 s, followed by 1.2 V for 10 s. The sample was then rinsed with deionized water (18.1 MΩ·cm) and dried under a stream of N_2.

To form a monolayer, a three-electrode cell comprising an oxidized gold working electrode, a platinum wire counter-electrode and a Ag/$AgNO_3$ (3 mM in ACN) reference electrode was used, and the potential was stepped from 0.3 V to -0.9 V, with 5 s at each potential, in the presence of a disulfide. Forty of these voltammetric pulses were applied to the electrode in a solution containing $[CH_3(CH_2)_{15}S]_2$ or $[CF_3(CF_2)_9(CH_2)_2S]_2$ (1 mM) and $LiClO_4$ (0.1 M) in tetrahydrofuran (THF). The sample was then removed from solution, rinsed with THF, and water, and dried under a stream of N_2.

X-ray Photoelectron Spectroscopy. Spectra were collected using a Scienta ESCA-300 spectrometer with monochromatized Al Kα X-rays generated using a rotating anode. Photoemission was measured with a 300-mm-diameter hemispherical analyzer. Samples were grounded by placing screws in contact with both electrode surfaces and the sample holder. The pressure in the sample chamber was $\sim 2\times10^{-9}$ Torr, and samples were analyzed at a 20° takeoff angle between the sample surface and the path to the analyzer. The pass energy for high-resolution spectra in the Au, O and S regions were 75 eV, 150 eV, and 300 eV, respectively, and the step energy for all high-resolution scans was 0.05 eV. Survey spectra were taken at a 300-eV pass energy and a step energy of 1 eV. High resolution Au spectra were referenced to the Au $4f_{7/2}$ peak, set at 84.0 eV, and intensities normalized to the largest Au $4f_{7/2}$ peak. High resolution S photoemission intensities were normalized to the largest sulfur $2p_{3/2}$ peak. Samples were analyzed by XPS within 1 h of monolayer formation, and the spectra were analyzed using CASAXPS® software.

Figure S1

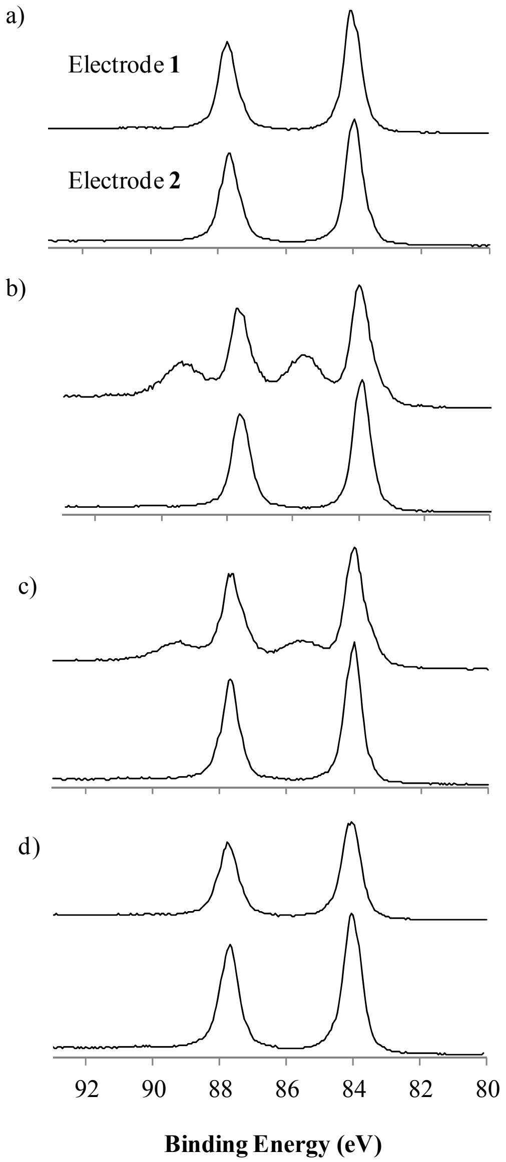

Fig. S1 High resolution x-ray photoelectron spectra of electrodes **1** and **2** in the Au 4f region: a) unmodified; b) after electrochemical oxidation of electrode **1**; c) after adsorption of a SAM on electrode **2** from $(C_{16}H_{33}S)_2$; and d) after reduction of the oxide coating on electrode **1**. Spectra were referenced to the Au $4f_{7/2}$ peak, set at 84.0 eV, and intensities normalized to the largest Au $4f_{7/2}$ peak.

Figure S2

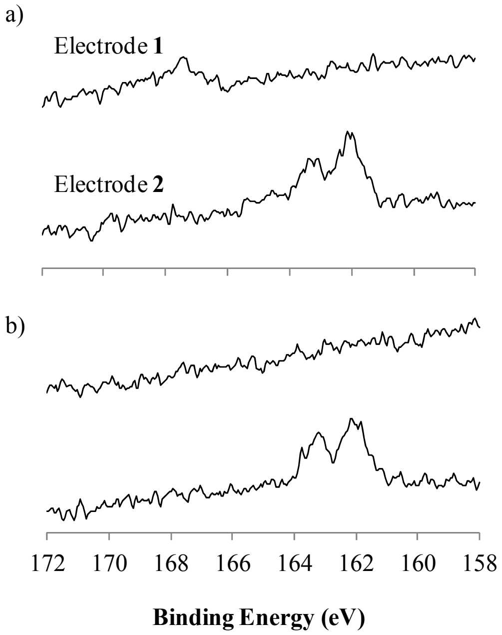

Fig. S2 High resolution x-ray photoelectron spectra of electrodes **1** and **2** in the sulfur 2p region: a) after adsorption of a SAM on electrode **2** from $(C_{16}H_{33}S)_2$; and b) after reduction of the oxide on electrode **1**. Intensities were normalized to the largest sulfur $2p_{3/2}$ peak.

Reference

[1] H. Ron, I. Rubinstein, *J. Am. Chem. Soc.* **1998,** *120*, 13444-13452.
[2] J. P. Labukas, T. J. H. Drake, G. S. Ferguson, *Langmuir*, 2010, **26**, 9497-9505.