Compatibility of ω-Functionality in the Electrochemically Directed Self-Assembly of Monolayers on Gold from Alkyl Thiosulfates

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Self-assembled monolayers were formed on gold electrochemically from ω-functionalized alkyl thiosulfates (Bunte salts). The resulting SAMs were characterized using X-ray photoelectron spectroscopy (XPS), contact-angle goniometry, and ellipsometry. A range of terminal functionality was examined, including CH_3, perfluoroalkyl, CO_2H, CO_2CH_3, $CONH_2$, CH_2OH, and vinyl groups. Side-reactions involving some of these functional groups were consistent with intermediates proposed in our earlier publications and begin to define the scope of this method for building chemical structures at interfaces.

Introduction

Self-assembled monolayers (SAMs) can be prepared on gold surfaces with ease from alkanethiols due to the low activation energy and large thermodynamic driving force for their chemisorption.[1,2] This method has allowed the convenient preparation of a variety of monolayers from solution, vapor, and even solid phase (i.e., lithography). The ubiquitous use of SAMs to prepare well-defined interfaces, pattern surfaces, direct cell growth, inhibit corrosion, immobilize oligonucleotides, and create nanoarrays clearly demonstrates their utility.[3−6] Although beneficial in many ways, the fast kinetics and stable structures also make the process of monolayer formation difficult to control regiochemically.

We have previously demonstrated that regioselective self-assembly can be achieved by applying anodic potentials to selected gold electrodes in solutions of alkyl thiosulfates (Bunte salts).[7−9] In the presence of tetrafluoroborate anion in THF, monolayer formation can be activated by application of a sufficiently oxidative potential (∼1 V) and occurs only at the active electrode. Oxidation appears to lead to S−S bond cleavage,[10] which liberates SO_3 and produces an alkyl sulfide radical that can bond to the gold surface.[11,12] Application of the anodic potential at a particular electrode, even when others are present, thus allows for control of where the monolayer forms. Methyl-terminated SAMs on gold surfaces, created electrochemically in this way, are nearly indistinguishable from those produced by the chemisorption of thiols.[11]

Our goal in the present study was to use this electrochemical approach to produce monolayers containing a variety of functional groups. Of particular interest were SAMs containing terminal methyl, fluorinated alkyl, carboxylic acid, ester, amide, hydroxyl, and vinyl groups. The primary question addressed by these studies is analogous to that routinely addressed by those developing synthetic methodology: What is the range of functionality that is chemically compatible with the electrosynthesis? Obviously some of these groups, notably vinyl and hydroxyl, could be expected to be reactive with the intermediates or byproducts of the electrosynthesis. Vinyl groups could be susceptible to electrophilic addition of sulfuric acid or bisulfite to give alkyl sulfates and to radical addition of an alkyl sulfide radical to create dialkyl sulfide linkages. Hydroxyl groups could react with any free SO_3 to make alkyl sulfate.

Alkyl thiosulfates containing terminal functionality can be easily synthesized by nucleophilic displacement of halide from the corresponding alkyl halide by thiosulfate ion ($S_2O_3^{2-}$), allowing for tailorable precursors to SAMs on gold. A variety of alkyl thiosulfates were prepared in this way in high yield. Although prone to hydrolysis, Bunte salts are stable in the absence of water and can be stored indefinitely at low temperature. If hydrolysis does occur, these compounds can be purified by rinsing or recrystallization. Elimination of any thiol or disulfide impurities was obviously important in these studies because they would lead to spontaneous chemisorption that would compete with the electrochemical process of interest. We have characterized the various functional SAMs prepared by electrochemisorption of alkyl thiosulfates using contact-angle goniometry, ellipsometry, and X-ray photoelectron spectroscopy (XPS).

Experimental Section

General. Tetrabutylammonium tetrafluoroborate (98%) and 12-bromo-1-dodecanol (98%) were obtained from TCI America and used as received. Ethanol (Anhydrous, J.T. Baker, 95%) was used as received. Acetonitrile (Acros, 99.8%) and tetrahydrofuran

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(THF, Mallinckrodt, 99%) were purified and dried using a Pure Solv system (Innovative Technology, Inc.). Silver nitrate (Fisher, 99.8%) was used as received. Water was purified with a Purelab Prima system (Elga) to a resistivity of ~0.3 MΩ cm. Hydrogen peroxide (30%), sulfuric acid (≥95%), and hydrochloric acid (GR) were used as received from EMD. 1-Iodo-1*H*,1*H*,2*H*,2*H*-perfluorododecane (97%), 1-bromohexadecane (98%), and sodium thiosulfate pentahydrate (99%) were used as received from Alfa Aesar. 11-Bromoundecanoic acid (Aldrich, 95%), 11-bromoundecanamide (Aldrich, 97%), undecyl-10-enyl bromide (98%, Lancaster), dodecanol (Aldrich, 98%), 1-dodecene (Fluka, >99%), 1-bromododecane (Aldrich, 97%), and tris(2-carboxyethyl)phosphine hydrochloride (TCEP, Thermo Scientific, ≥98%) were used without further purification. 11-Bromoundecanoic acid methyl ester was a gift from Professor Ned Hiendel in our department; its identity and purity were verified by NMR. Hexadecane (99%, Aldrich) was passed through activated alumina twice before use in contact-angle measurements. ^{1}H NMR spectra were collected with a Bruker 500 MHz spectrometer using methanol-d_4 (Cambridge Isotope Laboratories, Inc., 99.8%) as the solvent. Spectra were referenced to residual solvent protons at 3.30 ppm and are reported in units of δ ppm. Thermogravimetric analyses (TGA) were performed with a TA Instruments TGA 2950 thermogravimetric analyzer. Elemental analyses were done by Midwest Microlab, LLC, Indianapolis, IN.

Handling of Sodium Alkyl Thiosulfates. The synthesis of alkyl thiosulfates followed a procedure reported previously, with minor modifications.[7,13,14] Although these compounds appeared pure by NMR, even minute amounts of the corresponding thiol or disulfide could spontaneously adsorb on gold in a nonspecific manner. To remove any soluble thiol, the crystals were routinely stirred in CH_2Cl_2 for ~10 min, vacuum filtered, rinsed with CH_2Cl_2, and dried prior to use in electrochemical experiments and before TGA and elemental analyses. A notable decrease in the ease of dissolution of these compounds in THF after they had been dried *in vacuo* suggested that the as-prepared crystals may be hydrates. Thermogravimetric analyses, in which the temperature of the sample was raised from room temperature to 150 at 10 °C/min, were consistent with the presence of water of hydration. These measurements indicated a water content between 0.1 and 0.8 of an equivalent depending on the particular alkyl thiosulfate, which were not reproducible and may depend on relative humidity. As expected, the mass lost during TGA experiments decreased if the sample was first dried *in vacuo*. Any water of hydration was not included in mass calculations (*vide infra*).

$CH_3(CH_2)_{15}S_2O_3Na$. Sodium thiosulfate pentahydrate (2.48 g, 10.0 mmol) was dissolved in 40 mL of water and added to a solution of 1-bromohexadecane (3.06 g, 8.50 mmol) in 40 mL of ethanol. The mixture was refluxed until homogeneous (~20 h), cooled to room temperature, and vacuum filtered to remove the white solid product that had precipitated. Additional product was collected from the filtrate after removing some of the solvent by rotary evaporation and subsequently cooling in an ice bath. The crystalline product was combined, recrystallized twice from ethanol, and stored in a refrigerator. The isolated product yield was 96%. ^{1}H NMR: $CH_3(CH_2)_{15}SSO_3Na$, 0.89 (t, 3H); $CH_3(CH_2)_{13}$$CH_2CH_2SSO_3Na$, 1.28−1.40 (m, 27H); $CH_3(CH_2)_{13}$ $CH_2CH_2SSO_3Na$, 1.74 (m, 2H); $CH_3(CH_2)_{13}CH_2CH_2SSO_3Na$, 3.05 (t, 2H).

$CH_3(CH_2)_{11}S_2O_3Na$. Sodium thiosulfate pentahydrate (2.48 g, 10.0 mmol) was dissolved in 40 mL of water and added to a solution of 1-bromododecane (2.49 g, 8.20 mmol) in 40 mL of ethanol. The mixture was refluxed until homogeneous (~20 h), cooled to room temperature, and vacuum filtered to remove the white solid that had precipitated. Additional product was collected from the filtrate after removing some of the solvent by rotary evaporation and subsequently cooling in an ice bath. The crystalline product was combined, recrystallized twice from ethanol,

and stored in a refrigerator. The isolated product yield was 89%. ^{1}H NMR: $CH_3(CH_2)_{11}SSO_3Na$, 0.89 (t, 3H); $CH_3(CH_2)_9CH_2$-CH_2SSO_3Na, 1.28−1.40 (m, 18H); $CH_3(CH_2)_9CH_2CH_2SSO_3Na$, 1.74 (m, 2H); $CH_3(CH_2)_9$ $CH_2CH_2SSO_3Na$, 3.05 (t, 2H).

$CF_3(CF_2)_9(CH_2)_2S_2O_3Na$. Sodium thiosulfate pentahydrate (0.37 g, 1.49 mmol) was dissolved in 8 mL of water and added to a solution of 1-iodo-1*H*,1*H*,2*H*,2*H*-perfluorododecane (1.03 g, 1.50 mmol) in 24 mL of a 1:2 (v/v) mixture of ethanol and THF. The mixture was refluxed for 20 h and then cooled to room temperature. Solvent was removed by rotary evaporation, and the remaining white solid was recrystallized from ethanol, vacuum filtered, rinsed on the filter with cold water and then cold chloroform, dried under vacuum, and stored in a refrigerator. The isolated product yield was 92%. Elemental analysis: Anal. Calcd for $C_{12}H_4F_{21}O_3S_2Na$: C, 21.13; H, 0.59. Found: C, 20.79; H, 0.65. ^{1}H NMR: $CF_3(CF_2)_9CH_2CH_2SSO_3Na$, 2.77 (m, 2H); CF_3-$(CF_2)_9CH_2CH_2SSO_3Na$, 3.24 (m, 2H).

$HO_2C(CH_2)_{10}S_2O_3Na$. Sodium thiosulfate pentahydrate (2.48 g, 10.0 mmol) was dissolved in 40 mL of water and added to a solution of 11-bromoundecanoic acid (2.65 g, 8.30 mmol) in 40 mL of ethanol. The mixture was refluxed for 20 h and then cooled to room temperature. Solvent was removed by rotary evaporation, and the remaining white solid was recrystallized three times from ethanol, filtered, dried under vacuum, and stored in a refrigerator. The isolated product yield was 74%. ^{1}H NMR: $HO_2CCH_2CH_2(CH_2)_6CH_2CH_2SSO_3Na$, 2.26 (t, 2H); HO_2CCH_2-$CH_2(CH_2)_6CH_2CH_2SSO_3Na$, 1.59 (m, 2H); $HO_2CCH_2CH_2$-$(CH_2)_6CH_2CH_2SSO_3Na$, 1.31−1.41 (m, 12H); $HO_2CCH_2CH_2$-$(CH_2)_6CH_2CH_2SSO_3Na$, 1.75 (m, 2H); $HO_2CCH_2CH_2(CH_2)_6$-$CH_2CH_2SSO_3Na$, 3.05 (t, 2H).

$CH_3O_2C(CH_2)_{10}S_2O_3Na$. Sodium thiosulfate pentahydrate (2.48 g, 10.0 mmol) was dissolved in 40 mL of water and added to a solution of 11-bromoundecanoic acid methyl ester (2.65 g, 7.90 mmol) in 40 mL of ethanol. The mixture was refluxed for 20 h and then cooled to room temperature. Solvent was removed by rotary evaporation, and the remaining white solid was recrystallized three times with ethanol, filtered, dried under vacuum, and stored in a refrigerator. The isolated product yield was 81%. Elemental analysis: Anal. Calcd for $C_{12}H_{23}O_5S_2Na$: C, 43.10; H, 6.94. Found: C, 43.08; H, 6.80. ^{1}H NMR: $CH_3O_2CCH_2CH_2(CH_2)_6$-$CH_2CH_2SSO_3Na$, 3.64 (s, 3H); $CH_3O_2CCH_2CH_2(CH_2)_6CH_2$-$CH_2SSO_3Na$, 2.30 (t, 2H); $CH_3O_2CCH_2CH_2(CH_2)_6CH_2CH_2$-$SSO_3Na$, 1.59 (m, 2H); $CH_3O_2CCH_2CH_2(CH_2)_6CH_2CH_2SSO_3Na$, 1.30−1.40 (m, 12H); $CH_3O_2CCH_2CH_2(CH_2)_6CH_2CH_2SSO_3Na$, 1.74 (m, 2H); $CH_3O_2CCH_2CH_2(CH_2)_6CH_2CH_2SSO_3Na$, 3.05 (t, 2H).

$H_2NCO(CH_2)_{10}S_2O_3Na$. Sodium thiosulfate pentahydrate (2.48 g, 10.0 mmol) was dissolved in 40 mL of water and added to a solution of 11-bromoundecanamide (2.65 g, 8.30 mmol) in 40 mL of ethanol. The mixture was refluxed for 20 h and then cooled to room temperature. Solvent was removed by rotary evaporation, and the remaining white solid was recrystallized three times with ethanol vacuum filtered and stored in a refrigerator. The isolated product yield was 76%. Elemental analysis: Anal. Calcd for $C_{11}H_{22}NO_4S_2Na$: C, 41.36; H, 6.94. Found: C, 41.86; H, 6.99. ^{1}H NMR: $H_2NCOCH_2CH_2(CH_2)_6CH_2CH_2SSO_3Na$, 2.18 (t, 2H); $H_2NCOCH_2CH_2(CH_2)_6CH_2CH_2SSO_3Na$, 1.58 (m, 2H); $H_2NCOCH_2CH_2(CH_2)_6CH_2CH_2SSO_3Na$, 1.31−1.41 (m, 12H); $H_2NCOCH_2CH_2(CH_2)_6CH_2CH_2SSO_3Na$, 1.75 (m, 2H); $H_2NCOCH_2CH_2(CH_2)_6CH_2CH_2SSO_3Na$, 3.05 (t, 2H).

$HO(CH_2)_{12}S_2O_3Na$. Sodium thiosulfate pentahydrate (2.48 g, 10.0 mmol) was dissolved in 40 mL of water and added to a solution of 12-bromo-1-dodecanol (2.65 g, 8.30 mmol) in 40 mL of ethanol. The mixture was refluxed until homogeneous (~20 h), cooled to room temperature, and vacuum filtered to remove the white product that had precipitated. Additional product was collected from the filtrate after removing the solvent by rotary evaporation and recrystallizing the solid from ethanol. The two batches of crystalline product were then combined, recrystallized

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twice more with ethanol, and stored in the refrigerator. The isolated product yield was 92%. Elemental analysis: Anal. Calcd for $C_{12}H_{25}O_4S_2Na$: C, 44.98; H, 7.86. Found: C, 44.79; H, 7.72. ^{1}H NMR: HOCHCH$_2$(CH$_2$)$_8$CH$_2$CH$_2$SSO$_3$Na, 3.52 (t, 2H); HOCH$_2$CH_2(CH$_2$)$_8$CH$_2$CH$_2$SSO$_3$Na, 1.51 (m, 2H); HOCH$_2$-CH$_2$(CH_2)$_8$CH$_2$CH$_2$SSO$_3$Na, 1.30−1.40 (m, 17H); HOCH$_2$CH$_2$-(CH$_2$)$_8$CH_2CH$_2$SSO$_3$Na, 1.74 (m, 2H); HOCH$_2$CH$_2$(CH$_2$)$_8$CH$_2$-CH_2SSO$_3$Na 3.05 (t, 2H).

CH$_2$CH(CH$_2$)$_9$SSO$_3$Na. Sodium thiosulfate pentahydrate (2.38 g, 9.59 mmol) was dissolved in 40 mL of water and added to a solution of undecyl-10-enyl bromide (2.33 g, 8.00 mmol) in 40 mL of ethanol. The mixture was refluxed until homogeneous (~20 h) and cooled to room temperature, and the product was collected after removing all of the solvent by rotary evaporation. The crystalline product was recrystallized twice from ethanol, vacuum filtered until dry, and stored in the refrigerator. The isolated product yield was 92%. ^{1}H NMR: CHHCHCH$_2$(CH$_2$)$_6$-CH$_2$CH$_2$SSO$_3$Na, 4.94−5.00 (m, 1H); CHHCHCH$_2$(CH$_2$)$_6$CH$_2$-CH$_2$SSO$_3$Na, 4.88−4.92 (m, 1H); CHH CHHCH$_2$(CH$_2$)$_6$CH$_2$CH$_2$-SSO$_3$Na, 5.75−5.84 (m, 1H); CHHCHCH_2(CH$_2$)$_6$CH$_2$CH$_2$SSO$_3$Na, 2.03 (m, 2H); CHHCHCH$_2$(CH_2)$_6$CH$_2$CH$_2$SSO$_3$Na, 1.30−1.40 (m, 12H); CHHCHCH$_2$(CH$_2$)$_6$CH_2CH$_2$SSO$_3$Na, 1.73 (m, 2H); CHHCHCH$_2$(CH$_2$)$_6$CH$_2$CH_2SSO$_3$Na, 3.04 (t, 2H).

Preparation of Gold Substrates. Approximately 50 Å of titanium (as an adhesion promoter) and then ~2400 Å of gold were deposited on precut (~1 × 2 cm), piranha-cleaned glass microscope slides at 4 Å/s by electron-beam deposition (Indel Systems). *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.*

Electrosynthesis of SAMs. The electrosynthesis of SAMs followed our previously reported method, with minor modifications, using a Bioanalytical Systems BAS-100b potentiostat.[7,11] A standard three-electrode configuration was employed, with a gold substrate as the working electrode (~1 cm^2 immersed in solution), a platinum wire (1 mm × 30 mm) as the counter electrode, and a glass tube fitted with a vicor frit containing Ag/AgNO$_3$ (3 mM) and Bu$_4$NBF$_4$ (100 mM) in acetonitrile as the reference electrode. Monolayers were formed using 40 square-wave pulses, from −0.9 to 1.1 V for 5 s at each potential, in a solution containing 1 mM alkyl thiosulfate and 100 mM Bu$_4$NBF$_4$ in THF. Samples were removed from the cell, rinsed immediately with THF, ethanol, and water, and then dried in a stream of N$_2$. In each synthesis, an electrically isolated gold substrate was placed at the bottom of the electrochemical cell as a control to verify that no monolayer formed in the system spontaneously.

Contact-Angle and Ellipsometric Measurements. Advancing and receding contact angles of water (pH 7) and hexadecane were measured with a Rame-Hart NRL model 100 goniometer. Measurements were taken within 30 s after advancing or retracting the drop across the surface, with a minimum of six measurements at three different spots per sample. The approximate volume of the drops used to measure advancing angles was 2 μL. We use the term "wetting" to describe any drop with a contact angle of less than 10°. Ellipsometric measurements were made using a Rudolph Auto-EL III automatic nulling ellipsometer equipped with a helium−neon laser (λ = 632.8 nm) at an angle of incidence of 70°. For a given sample, the optical constants of freshly evaporated gold were measured first, the SAM was electrochemically deposited on the surface, and then the sample was reanalyzed at three different spots. The manufacturer's software was used to measure optical constants (program 27) and calculate thickness (program 213), assuming a single overlayer on the gold substrate. A refractive index of 1.45 was assumed for all SAMs.

X-ray Photoelectron Spectroscopy. Spectra were collected using a Scienta ESCA-300 spectrometer. Monochromatic Al Kα X-rays were generated using a rotating anode and photoemission monitored with a 300 mm diameter hemispherical analyzer. Gold samples were grounded by placing a screw in contact with both their surface and the sample holder. The pressure in the sample chamber was ~2×10^{-9} Torr, and unless otherwise noted, samples were analyzed at a 20° takeoff angle between the sample surface and the path to the analyzer. Calibration of the data was performed by setting the position of the Au 4f$_{7/2}$ peak at 84.0 eV. The pass energy for high-resolution spectra in the Au 4f and F 1s regions was 75 eV, and for all other elements it was 300 eV. The step energy for all high-resolution scans was 0.05 eV. Survey spectra were taken using a 300 eV pass energy and a step energy of 1 eV. Samples were analyzed by XPS within 1 h of monolayer formation.

The intensity of the high-resolution C 1s photoemission was the sum of five scans for each SAM except the monolayer derived from CH$_3$(CH$_2$)$_{11}$S$_2$O$_3$Na, which was the sum of eight scans. The intensity of the S 2p photoemission was the sum of eight scans for each SAM except the TCEP-treated monolayer derived from H$_2$NCO(CH$_2$)$_{10}$S$_2$O$_3$Na, which was the sum of six scans. The intensity of the O 1s photoemission was the sum of eight scans for the SAM derived from HO$_2$C(CH$_2$)$_{10}$S$_2$O$_3$Na, six for that derived from CH$_3$O$_2$C(CH$_2$)$_{10}$S$_2$O$_3$Na, five scans for that from H$_2$NCO(CH$_2$)$_{10}$S$_2$O$_3$Na, and eight scans for that from HO-(CH$_2$)$_{12}$S$_2$O$_3$Na.

Results and Discussion

The formation of SAMs via oxidation of alkyl thiosulfates at gold electrodes has been reported previously by our group.[7,11] Using nucleophilic substitution reactions, we have now synthesized several ω-functionalized alkyl thiosulfates, X(CH$_2$)$_n$SSO$_3$-Na (eq 1)

$$X(CH_2)_nBr + Na_2S_2O_3 \rightarrow X(CH_2)_nS_2O_3Na + NaBr \quad (1)$$
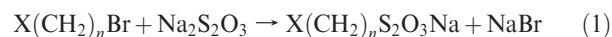
where X = CH$_3$, n = 11, 15; CO$_2$H, n = 10; CO$_2$CH$_3$, n = 10; CONH$_2$, n = 10; OH, n = 12; and HC=CH$_2$, n = 9. A fluorinated compound, X = n-C$_{10}$F$_{21}$, n = 2, was prepared from the iodide instead of the bromide. We optimized the protocol used for the electrosynthesis of SAMs from each of these Bunte salts, with respect to both applied electrical potential and the number of square-wave pulses used to form the SAMs. In these experiments, we used the contact angles of hexadecane and of water on the product SAMs to assess their quality. To optimize the oxidation potential, monolayers were formed using 10 square-wave pulses, starting at −0.9 V and ending at potentials in the range of 0.8−1.3 V, in 0.1 V increments. We then studied the number of pulses at the optimal potential necessary to form a good monolayer. In the course of these experiments, we found that 40 square-wave pulses between −0.9 and 1.1 V were generally applicable for the preparation of the SAMs of interest and that an additional 40 pulses did not disrupt the SAMs once formed.

Methyl-Terminated SAMs. Methyl-terminated SAMs were prepared electrochemically from either hexadecyl or dodecyl thiosulfate (C$_{16}$ and C$_{12}$, respectively). The contact angle of hexadecane on the C$_{16}$ monolayer was 45°, in agreement with our previous report,[7] as well as with measurements made on SAMs adsorbed from hexadecanethiol in our laboratories and those of others (Table 1). The contact angle of water on this surface (111°) was slightly lower than reported for the analogous SAM adsorbed from thiol (116°). The ellipsometric thickness of this SAM was ~14 Å, again in agreement with our previous report. The thickness of a SAM formed by adsorption of hexadecanethiol in our laboratory, however, was about 6 Å thicker than this value. Tables 1 and 2 provide values of contact angle and ellipsometric thickness reported for analogous SAMs adsorbed from thiols and disulfides.

Table 1. Contact Angles (deg) on Gold-Supported SAMs Derived Electrochemically from Alkyl Thiosulfates, RS$_2$O$_3$Na, with Data for SAMs Adsorbed from the Corresponding Thiols for Comparison[a]

| | θ_a (θ_r) | | | |
| | hexadecane | | water | |
R	Bunte salt	thiol	Bunte salt	thiol
(CH$_2$)$_{15}$CH$_3$	45 (37)	45[41] (40)[41]	111 (90)	116[41] (104)[41]
(CH$_2$)$_{11}$CH$_3$	38 (17)	45[1] (nr)	108 (87)	112[1] (nr)
(CH$_2$)$_2$(CF$_2$)$_9$CF$_3$	80 (73)	78[42] (58)[42]	125 (114)	112.6 −120[42−47] (105−109)[42,45,46]
(CH$_2$)$_{10}$CO$_2$H	<10 (<10)	<10−15[48−50] (nr)	56 (38)	<5−40[1,39−44] (24)[49]
(CH$_2$)$_{15}$CO$_2$H		0[1](nr)		0−72[1,51] (nr)
(CH$_2$)$_{10}$CO$_2$CH$_3$	<10 (<10)	28−38[1,48,50] (25)[48]	74 (58)	67−74[1,48,50,52] (61)[48]
(CH$_2$)$_{10}$CONH$_2$	<10 (<10)	<10[48,50] (nr)	38 (<10)	<15[43,44,48,50,53] (nr)
(CH$_2$)$_{12}$OH	<10 (<10)		39−55 (<10)	
(CH$_2$)$_{11}$OH		<10[1,50] (nr)		0−34.2[1,43,50,54−57] (<5−32)[1,54]
(CH$_2$)$_9$CH=CH$_2$	<10 (<10)	38[52] (nr)	89 (62)	103−108[52,58] (nr)

[a] nr = not reported.

Table 2. Ellipsometric Thickness on Gold-Supported SAMs Derived Electrochemically from Alkyl Thiosulfates, RS$_2$O$_3$Na, with Data for SAMs Adsorbed from the Corresponding Thiols and Disulfides for Comparison[a]

R	SAMs from Bunte salts (Å)	SAMs from thiols (Å)	SAMs from disulfides (Å)
(CH$_2$)$_{15}$CH$_3$	14	20[41]	17,[41] 19[59]
(CH$_2$)$_{11}$CH$_3$	4	15[1]	
(CH$_2$)$_2$(CF$_2$)$_9$CF$_3$	14		16[59]
(CH$_2$)$_2$(CF$_2$)$_9$CH$_3$		19[37,b]	
(CH$_2$)$_{10}$CO$_2$H	13	15[1]	16[59]
(CH$_2$)$_{10}$CO$_2$CH$_3$	2−11		
(CH$_2$)$_{10}$CONH$_2$	15		
(CH$_2$)$_{12}$OH	74 ± 33		
(CH$_2$)$_{11}$OH		11,[54,56] 16,[57] 13[60]	11[54]
(CH$_2$)$_9$CH=CH$_2$	10		

[a] The manufacturer reports an instrumental error of ±3 Å. [b] Thickness estimated from surface plasmon resonance measurements.

A perusal of Table 2 reveals that the ellipsometric thickness for all of the SAMs reported in this paper are lower than those reported for SAMs adsorbed from thiols. This systematic difference may reflect a slightly lower packing density associated with these SAMs compared to those formed from thiols.[11] We infer that steric hindrance may be important as the hydrated thiosulfate groups approach the gold surface through a nearly complete monolayer. An additional factor, described previously by others,[1,15,16] should also be considered when interpreting ellipsometric data: optical constants are typically collected for the gold substrate prior to SAM formation, and these constants are assumed to characterize the nominally "bare" substrate. When measured in air, however, these constants include the effect of weakly adsorbed contaminants that are displaced when the SAM adsorbs. As a result, the measured differences upon SAM formation are smaller than would be expected if the substrate were actually bare beforehand. In the course of our experiments, we noticed that during the first few hours after a gold deposition the imaginary component of the refractive index of the gold substrate usually decreased, sometimes dramatically. These changes are consistent with adsorption of contaminants from air, which would affect the measured thickness. A range of monolayer thicknesses have been reported in the literature for SAMs on gold, and differences are often ascribed either to removal of physisorbed contamination or

to use of different physical models to treat the ellipsometric data.[1,15,16]

The SAM derived from CH$_3$(CH$_2$)$_{11}$S$_2$O$_3$Na had a contact angle of hexadecane (38°) that was about 15% lower than that on a SAM adsorbed from the corresponding thiol. Interestingly, the contact angles of water on these two surfaces were almost the same (108° vs 112°). Monolayers with shorter alkyl chains are known to be less ordered,[17] and this tendency may be amplified for SAMs formed from thiosulfates due to the slightly lower packing density. The ellipsometric thickness of this SAM was also lower than one adsorbed from the corresponding thiol (Table 2), again consistent with a less dense monolayer.

Analyses of the C$_{16}$ and C$_{12}$ monolayers by X-ray photoelectron spectroscopy (XPS) revealed the presence of gold, carbon, and sulfur, as expected. High-resolution spectra in the C 1s region contained a single peak for both the hexadecyl (284.6 eV, fwhm 1.10 eV) and dodecyl (284.5 eV, fwhm 1.16 eV) cases (Figure 1).[1] A high-resolution spectrum in the sulfur 2p region of the C$_{16}$ SAM contained the expected spin−orbit doublet at 161.8 and 163.0 eV with a full width for each component of 0.88 eV (Figure 2). Although the spectrum appears similar to those reported in the literature for similar SAMs,[18−20] the photoemission envelope could not be adequately fit with a single 2:1 doublet. Addition of a second doublet at 163.1 and 164.3 eV (set to same fwhm as the primary doublet) allowed a good fit and accounted for ∼25% of the total sulfur. It is possible that this additional doublet may be present in other XPS spectra of SAMs in the literature but is more easily apparent with the high resolution and signal-to-noise afforded by the Scienta-300 spectrometer. The primary S 2p spin−orbit doublet for the C$_{12}$ monolayer appeared at 161.8 and 163.0 eV (fwhm 0.81 eV), and the secondary doublet (163.1 and 164.2 eV) accounted for about 27% of the total sulfur on that surface (Figure 2). The C:S ratios of 27:1 (C$_{16}$) and 18:1 (C$_{12}$) reflect attenuation[21,22] of the S photoemission by the intervening alkyl chain.

The additional spin−orbit doublet (∼163.1 and ∼164.2 eV) is present in the sulfur 2p spectra for most of the SAMs presented in this paper and is similar in binding energy to peaks attributed by

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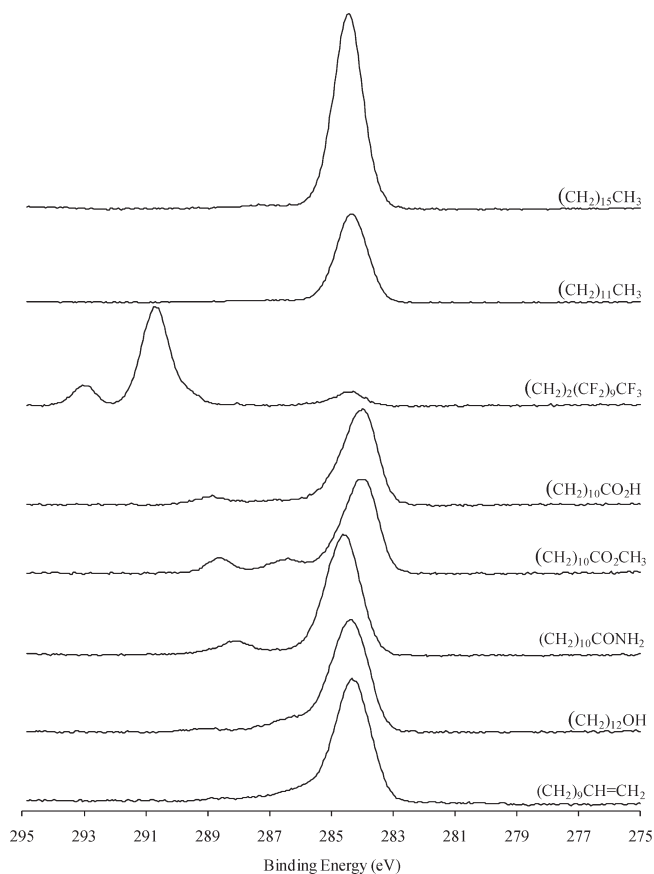
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Figure 1. High-resolution X-ray photoelectron spectra in the carbon 1s region for monolayers derived from alkyl thiosulfates, RS_2O_3Na, with R = $CH_3(CH_2)_{15}$, $CH_3(CH_2)_{11}$, $CF_3(CF_2)_9(CH_2)_2$, $HO_2C(CH_2)_{10}$, $CH_3O_2C(CH_2)_{10}$, $H_2NCO(CH_2)_{10}$, $HO(CH_2)_{12}$, and $CH_2CH(CH_2)_9$. The intensities were scaled, as necessary, to the same number of scans so that they could be compared.

others to radiation-induced damage during measurement,[23−27] to unbound thiols and disulfides,[27−30] or to dialkyl sulfide species.[24] Although small amounts of thiol or disulfide could be formed under our experimental conditions,[14] conversion to dialkyl sulfides is unlikely. Another possible source of additional peaks in XPS spectra of SAMs on gold is the position of thiolate atoms with respect to the lattice structure of the gold surface.[31,32] Many studies have found that the S atoms prefer 3-fold hollow sites (fcc) on the gold surface, but recent two-site models also suggest the

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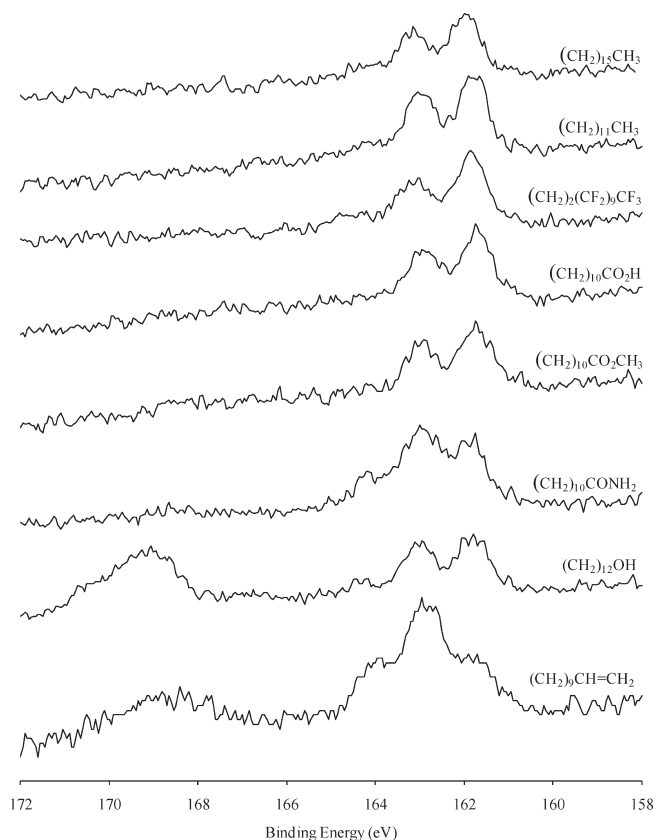
Figure 2. High-resolution X-ray photoelectron spectra in the sulfur 2p region for monolayers derived from alkyl thiosulfates, RS_2O_3Na, with R = $CH_3(CH_2)_{15}$, $CH_3(CH_2)_{11}$, $CF_3(CF_2)_9(CH_2)_2$, $HO_2C(CH_2)_{10}$, $CH_3O_2C(CH_2)_{10}$, $H_2NCO(CH_2)_{10}$, $HO(CH_2)_{12}$, and $CH_2CH(CH_2)_9$.

possibility of sulfur sites almost on top of individual gold atoms.[33] In addition, the size of gold crystallites as well as the relative amounts of the primary (111) texture and secondary (100) texture may vary for evaporated gold films produced under different conditions in different laboratories.[34] Finally, the possibilities of two sulfur atoms bound to a single gold adatom as well as a single sulfur bridging two gold atoms have been proposed.[35] The connection between these possible structural variations and sulfur 2p binding energies in XPS are not yet understood.

In control experiments designed to test some of these hypotheses, we monitored spectra as a function of X-ray dosage in our spectrometer and found that X-ray-induced damage does not appear to be responsible for the additional S 2p doublet. To learn whether the additional doublet is specific to SAMs formed electrochemically from alkyl thiosulfates or is also present in spectra of SAMs adsorbed from thiols, we collected XPS data for a SAM adsorbed from an ethanolic solution of hexadecanethiol (1 mM). This spectrum also contained the extra doublet, albeit at lower intensity (13% of the photoemission). We infer that the slightly lower packing density of SAMs formed electrochemically[7] may be related to the higher intensity of the additional S 2p doublet. These results narrow the likely sources of the additional

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photoemission either to unbound thiols or disulfides[18,28,36] or structural differences at the gold—sulfur interface.

Fluorinated Alkyl SAMs. Monolayers formed from a fluorinated Bunte salt, $CF_3(CF_2)_9(CH_2)_2S_2O_3Na$, were both hydrophobic ($\theta_a = 125°$ with H_2O) and oleophobic ($\theta_a = 80°$ with hexadecane), consistent with literature reports for similar SAMs adsorbed from thiols (Table 1). The ellipsometric thickness of this SAM (14 Å), however, was a few angstroms lower than that reported for a structurally similar SAM adsorbed from a thiol (Table 2), again consistent with a slightly less compact monolayer.

A survey XPS spectrum of this SAM confirmed the presence of carbon, gold, sulfur, and fluorine. A high-resolution spectrum in the carbon 1s region contained peaks assignable to CF_3 at 293.2 eV, CF_2 at 290.9 eV, and CH_2 at 284.5 eV, with full widths at half-maximum of 0.89, 1.04, and 1.01 eV, respectively (Figure 1).[37] An adequate fit to the data, however, required addition of two small shoulders at 289.7 and 285.4 eV, presumably corresponding to the CF_2 and CH_2 carbons that are adjacent to one another. The sulfur 2p region contained a doublet at 161.8 and 163.0 eV (fwhm, 0.86 eV) characteristic of gold-bound thiolate as well as a second doublet at 163.5 and 164.7 eV as discussed for the other SAMs (*vide supra*) accounting for about 23% of the total sulfur photoemission (Figure 2). A high-resolution spectrum in fluorine 1s region contained a peak at 688.3 eV with a full width at half-maximum of 1.55 eV.

Carboxylic Acid-Terminated SAMs. Monolayers derived from a carboxylic acid-terminated Bunte salt, $HO_2C(CH_2)_{10}$-S_2O_3Na, had an advancing contact angle of water of 56° (Table 1), which is significantly higher than that reported for an analogous SAM adsorbed from the corresponding thiol. As expected, this surface was wet by hexadecane. Nonetheless, the ellipsometric thickness (13 Å) was close to that reported for an analogous SAM formed from the corresponding thiol (Table 2).

A survey XPS spectrum confirmed the presence of carbon, gold, sulfur, and oxygen. High-resolution XPS in the C 1s region of this monolayer was fit with three peaks: 284.2 eV (fwhm, 1.26 eV), assigned to the alkyl chain; 285.7 eV (fwhm, 1.93 eV), assigned to the α-carbon adjacent to the carboxyl group; and 288.9 eV (fwhm, 1.93 eV), assigned to the carboxyl carbon (Figure 1).[1] As with the other SAMs, a high-resolution spectrum in the sulfur 2p region contained a primary doublet assigned to gold-bound thiolate (161.7 and 162.9 eV; fwhm, 0.83 eV) and a secondary doublet at 163.0 and 164.1 eV, in this case corresponding to ~20% of the total S 2p photoemission (Figure 2). A high-resolution spectrum of the oxygen 1s region contained two peaks, assigned to the carbonyl oxygen at 532.4 eV (fwhm, 1.93 eV) and the hydroxyl oxygen at 533.7 eV (fwhm, 1.33) (Figure 3).

Methyl Ester-Terminated SAMs. A SAM derived from $CH_3O_2C(CH_2)_{10}S_2O_3Na$ was wet by hexadecane, whereas advancing contact angles of 28°–38° were reported for an analogous SAM adsorbed from the corresponding thiol (Table 1). The advancing contact angle of water, however, was the same as that reported for the analogous SAM adsorbed from the corresponding thiol (Table 1). The ellipsometric thickness of this SAM (~2–11 Å) was lower than expected for a densely packed monolayer but also varied from sample to sample.

X-ray photoelectron spectroscopy confirmed the presence of the carboxylate ester functionality at the surface.[1,38] A survey
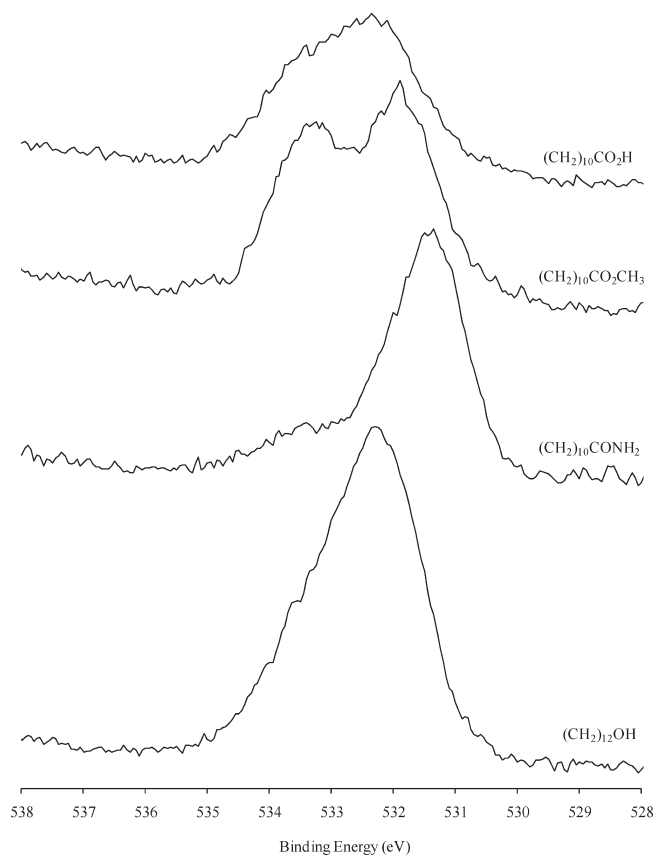
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Figure 3. High-resolution X-ray photoelectron spectra in the oxygen 1s region for monolayers derived from alkyl thiosulfates, RS_2O_3Na, with R = $HO_2C(CH_2)_{10}$, $CH_3O_2C(CH_2)_{10}$, H_2NCO-$(CH_2)_{10}$, and $HO(CH_2)_{12}$. The intensities were scaled, as necessary, to the same number of scans so that they could be compared.

spectrum contained carbon, gold, sulfur, and oxygen. A high-resolution spectrum in the carbon 1s region contained peaks assigned to the carboxyl carbon at 288.8 eV (fwhm, 0.99 eV), the methyl carbon of the ester group at 286.6 eV (fwhm, 1.52 eV), the α-carbon at 285.1 eV (fwhm, 085 eV), and the other carbon atoms of the alkyl group at 284.2 eV (fwhm, 1.19 eV) (Figure 1).[1] The ratio of photoemission intensity from the carbonyl carbon to the methyl carbon was approximately 1:1. The sulfur 2p region contained a doublet at 161.7 and 162.9 eV (fwhm, 0.88 eV) characteristic of gold-bound thiolate as well as a second doublet at 163.1 and 164.3 eV as discussed for the other SAMs (*vide supra*) accounting for about 22% of the total sulfur photoemission (Figure 2). A high-resolution spectrum in the oxygen 1s region revealed the presence of two types of oxygen: one assigned to the carbonyl oxygen (532.0 eV; fwhm, 1.52 eV) and the other to the ether oxygen (533.6 eV; fwhm, 1.28 eV) (Figure 3). The ratio of carbonyl oxygen to ether oxygen is ~1.5:1, which may indicate a preferred orientation of this group at the surface.

Amide-Terminated SAMs. Monolayers derived from an amide-terminated Bunte salt, $H_2NCO(CH_2)_{10}S_2O_3Na$, had an advancing contact angle of water of 38° (Table 1), which was higher than that reported for an analogous SAM adsorbed from the corresponding thiol (<15°). As expected, this surface was wet by hexadecane. The ellipsometric thickness of this monolayer was 15 Å, consistent with a single layer of adsorbate.

A survey XPS spectrum of this SAM confirmed the presence of carbon, oxygen, nitrogen, and sulfur on the gold surface, consistent with the molecular precursor.[38] A high-resolution spectrum in the carbon 1s region contained peaks assigned to the

carbonyl carbon of the amide group at 288.2 eV (fwhm, 1.54 eV), the α-carbon at 285.6 eV (fwhm, 1.54 eV), and the other carbon atoms of the alkyl chain at 284.7 eV (fwhm, 1.23 eV) (Figure 1).[38] The high-resolution spectrum of the sulfur 2p region was more complex than expected, with three prominent peaks. These peaks could be fit with two spin−orbit doublets of approximately the same intensity, assigned to thiolate (∼54%; 161.8 and 163.0 eV; fwhm, 1.07 eV) and to a secondary species (∼46%; 163.0 and 164.2 eV; fwhm, 1.07 eV) (Figure 2). High-resolution scans of the oxygen 1s (Figure 3) and nitrogen 1s regions contained peaks assigned to the oxygen (531.5 eV; fwhm, 1.44 eV) and the nitrogen (399.8 eV; fwhm, 1.44 eV) of the primary amide as well as a broad unresolved peak due to an additional oxygen species (533.1 eV; fwhm, 2.52 eV; 30% of the O 1s photoemission). The ratio of intensities for (primary) oxygen and nitrogen photoemission from the amide functionality, corrected by the relative sensitivity factors, was close to 1:1.

The large amount of secondary, low oxidation-state sulfur, as well as the additional O 1s peak, led us to consider the possible presence of a thin, hydrogen-bonded adlayer on top of the SAM. Such an adlayer could comprise tangled disulfide molecules, $[H_2NCO(CH_2)_{10}S]_2$—an expected byproduct of the electrosynthesis—held to the surface by hydrogen bonding at two locations. To test this hypothesis, we soaked the SAM in a 5 mM solution of tris(2-carboxyethyl)phosphine (TCEP) for 1 h with the hope of reducing any disulfides present and thereby making the presumed adlayers easier to remove. Consistent with our hypothesis, this treatment followed by rinsing with water nearly eliminated the secondary sulfur species from the XPS spectrum (Figure 4). The XPS spectrum of the treated surface showed what appeared to be a clean doublet due to thiolate sulfur at 161.7 and 162.9 eV (fwhm, 0.91 eV). In order to properly fit the spectrum, only a small amount of an additional sulfur species, comprising 12% of the total sulfur, was needed at 162.9 and 164.1 eV. The thickness of the monolayer was unchanged as a result of this treatment, indicating that the amount of material removed was not large. The contact angle of water, however, decreased from 38° to about 30°, consistent with the removal of a hydrophobic component.

Hydroxyl-Terminated SAMs. The SAM produced from $HO(CH_2)_{12}S_2O_3Na$ was hydrophilic, with an advancing water contact angle of 39°−55°, but its ellipsometric thickness was larger than would be expected for a hydroxyl-terminated SAM and varied greatly from sample to sample (74 ± 33 Å). We therefore used angle-resolve XPS to provide an independent measurement of the thickness. High-resolution spectra in the Au $4f_{7/2}$ region were collected at takeoff angles of 10°, 15°, 20°, 25°, 30°, and 90° between the detector and the plane of the sample. To normalize the intensity data, spectra were collected for the gold substrate both with the SAM in place and after it had been sputtered with Ar ions until free of carbon. The normalized intensity increased with increasing takeoff angle (φ), as predicted by eq 2

$$\ln(I/I_0) = -d/\lambda \sin \varphi \qquad (2)$$

where I is the intensity measured through the monolayer, I_0 is that measured on clean gold (assumed to be infinitely thick), λ is the attenuation length for a gold $4f_{7/2}$ photoelectron through a hydrocarbon overlayer, and d is the film thickness. Assuming an attenuation length of 40 Å,[39] a plot of $\ln(I/I_0)$ as a function
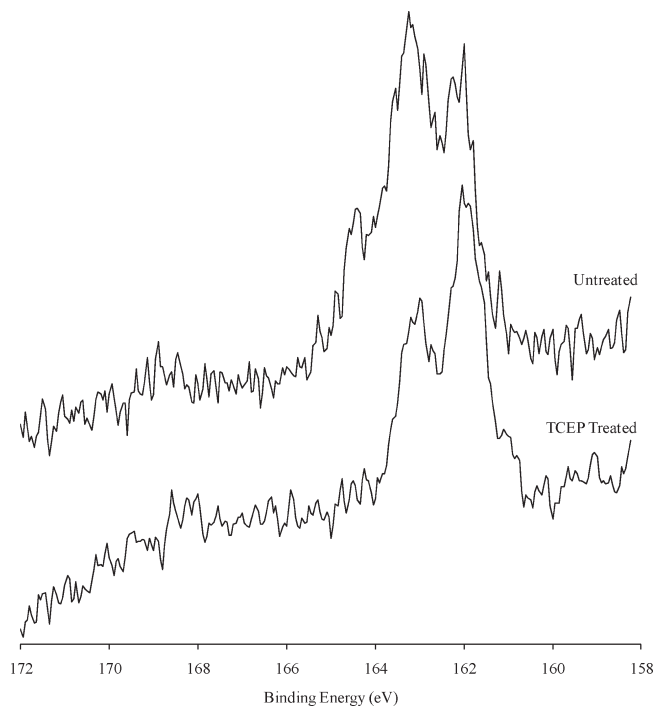

Figure 4. High-resolution X-ray photoelectron spectra in the sulfur 2p region for a monolayer derived from $H_2NCO(CH_2)_{10}$-S_2O_3Na and the same monolayer after treatment with tris(2-carboxyethyl)phosphine hydrochloride (TCEP). The intensities were scaled, as necessary, to the same number of scans so that they could be compared.

of $1/\sin \varphi$ was linear for takeoff angles above 15° and gave a SAM thickness of 29 Å. We surmise that the increased thickness of this film may reflect bi- or multilayer formation due to side reactions. The ellipsometric results may be complicated by adsorption of water by sulfate groups at the surface. These measurements could also be affected by inadequacies of either the assumed refractive index or the single-overlayer model used to calculate thickness for a film with a significant concentration of sulfate groups at its surface, though these effects should be small.

A survey XPS spectrum contained oxygen, carbon, and sulfur photoemission, in addition to that of the gold substrate. As expected, a scan of the sulfur 2p region contained not only a spin−orbit doublets for thiolate (161.8 and 163.0 eV; fwhm, 0.90 eV) and the secondary sulfur species observed for the other SAMs (163.2 and 164.4 eV), but also a broad, unresolved peak due to sulfate (169.3 eV) that accounted for nearly half of the total S 2p photoemission (Figure 2). We had anticipated that the hydroxyl group might react with SO_3—produced as a byproduct of the electrochemistry—to produce surface-bound alkyl sulfate. Angle-resolved XPS indicated a higher concentration of sulfate at the surface of the monolayer, with thiolate beneath, bound to gold. A high-resolution spectrum in the oxygen 1s region was best fit with two peaks (Figure 3): one assigned to hydroxyl at 532.3 eV (fwhm, 1.47 eV) and the other to sulfate at 533.5 eV (fwhm, 1.73 eV) (Figure 3), confirming the presence of the latter.[40] A high-resolution scan of the carbon 1s region contained peaks corresponding to the aliphatic chain at 284.5 eV (fwhm, 1.32 eV) and the hydroxyl/sulfate carbon at 286.1 eV (fwhm, 2.33 eV) (Figure 1).[1,38] The broadening of this peak is likely due to the

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presence of both hydroxyl- and sulfate-bound carbon.[1,38,40] There was also a minor peak corresponding to ~3% of the C 1s photoemission at 289.3 eV (fwhm, 1.45 eV), consistent with a small amount of carboxylic acid.

To determine whether the sulfate was hydrolytically labile, we soaked this SAM in 0.1 M HCl for 1 h and then reanalyzed the surface by XPS. Although the contact angle of water decreased from 39° to 55° to 30° as a result of this treatment, the ellipsometric thickness did not change. Furthermore, an XPS spectrum of the sulfur 2p region still indicated that about 50% of the total sulfur photoemission was due to sulfate, consistent with those species still being bound to the SAM. Curiously though, this treatment decreased the amount of thiolate sulfur relative to the secondary sulfur species, perhaps indicating a structural change at the gold−SAM interface. The nature of these spectroscopic changes is a focus of ongoing study.

As a control experiment to demonstrate the plausibility of nucleophilic capture of SO_3 by hydroxyl groups in this system, we performed the electrosynthesis using hexadecyl thiosulfate, which has no hydroxyl group, in the presence of a 10-fold excess of dodecanol so that any free alkyl sulfate produced could be concentrated and analyzed by NMR (eq 3). After 300 potentiometric pulses, the gold electrode was removed

$$CH_3(CH_2)_{15}S_2O_3Na + CH_3(CH_2)_{11}OH \xrightarrow[1.1\ eV]{Au} SAM$$

$$+ CH_3(CH_2)_{11}OSO_3Na \qquad (3)$$
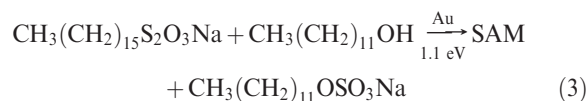
from the solution and then the solvent was removed by rotary evaporation. The resulting crude solid was dissolved in deuterated methanol and a ^{1}H NMR spectrum collected. The spectrum

contained a small triplet (3.97 ppm), consistent with the presence of sodium dodecyl sulfate.

Vinyl-Terminated SAMs. Monolayers derived from $CH_2CH(CH_2)_9S_2O_3Na$ were wet by hexadecane. A SAM adsorbed from the corresponding thiol $CH_2CH(CH_2)_9SH$ was reported to have a finite contact angle (Table 1). Likewise, the contact angle of water on this surface was lower than those reported for corresponding SAMs formed from thiols (89° vs 103°−108°). The ellipsometric thickness of this SAM was slightly lower than that of other SAMs formed from alkyl thiosulfates with a similar number of carbon atoms (Table 2).

We used XPS to examine the reason for these differences in wettability. A survey scan confirmed the presence of carbon, sulfur, and gold but also showed a significant amount of oxygen.[38] A high-resolution scan of the sulfur 2p region revealed a complex envelope centered at ~162.9 eV, consistent with low oxidation states, but also contained a broad peak at 168.7 eV, indicating the presence of sulfate (Figure 2). The envelope at lower binding energy could be fit with two spin−orbit doublets: one for the thiolate bound to gold (161.7 and 162.9 eV; fwhm, 1.00 eV; 35%) and the other consistent with the "secondary species" found for the other SAMs (162.9 and 164.1 eV; 65%). In this case, however, the higher binding energy doublet is the major component. The binding energy of this doublet is consistent with the presence of dialkyl sulfide moieties, which could be formed by the addition of an alkyl sulfide radical (a presumed intermediate in the electrosynthesis) to the vinyl group of the adsorbate. Such a byproduct could explain the prominence of this doublet, relative to that corresponding to the gold-bound thiolate. The presence of sulfate is consistent with the oxygen photoemission and wettability and indicates the addition of bisulfate or sulfuric acid—byproduct of the electrochemistry—across the carbons of the vinyl group. Any unbound inorganic salts (e.g., $NaHSO_4$, Na_2SO_4) would have been removed by the water rinse prior to collecting the spectrum.[11] A high-resolution scan of the carbon 1s region contained a peak corresponding to the aliphatic chain at 284.5 eV (fwhm, 1.28 eV) and a broad peak assigned the carbon bound to sulfate at 285.9 eV (fwhm, 2.85 eV) (Figure 1). There was also a minor peak corresponding to ~3% of the C 1s photoemission at 288.6 eV (fwhm, 1.93 eV) consistent with a small amount of carboxylic acid.

Conclusions

Self-assembled monolayers were formed electrochemically from alkyl thiosulfates having a range of terminal functionality. Although most of these precursors—methyl, carboxylic acid, ester, primary amide, perfluoroalkyl—gave the corresponding SAMs, side reactions between byproducts of the electrosynthesis and terminal hydroxyl and vinyl groups gave a mixture of products. Analysis of the SAMs by XPS, contact angle goniometry, and ellipsometry was consistent with our previous characterization of SAMs formed electrochemically as being analogous but slightly less dense than those formed from thiols.[7] Detailed analysis of sulfur 2p photoemission spectra revealed evidence for two types of sulfur within monolayers formed electrochemically or by chemisorption of thiol, and assignment of the secondary species is a topic of continuing interest in our group. The results described in this paper begin to define the scope of applicability of this method of SAM formation with respect to chemical functionality and therefore lay the groundwork for its use in future scientific studies or technological applications.

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Supporting Information Available: High-resolution X-ray photoelectron spectra in the S 2p, C 1s, and O 1s regions with the curve fitting to provide peak positions, full widths at half-maximum, and percent composition. This material is available free of charge via the Internet at http://pubs.acs.org.