

Electrochemical Self-Assembly of Monolayers from Alkylthiosulfates on Gold

Mong-Tung Lee,[†] Chen-Chan Hsueh,[†] Michael S. Freund,^{*,†} and Gregory S. Ferguson^{*,†,‡}

Departments of Chemistry and Materials Science & Engineering, Lehigh University, Bethlehem, Pennsylvania 18015-3172

Received July 31, 2002. In Final Form: February 3, 2003

Selective preparation of self-assembled monolayers (SAMs) on gold was accomplished by electrolysis of alkylthiosulfates (Bunte salts) in tetrahydrofuran in the presence of tetrabutylammonium tetrafluoroborate as the supporting electrolyte. Tetrafluoroborate ions inhibited the spontaneous chemisorption of alkylthiosulfates to form monolayers, so that monolayers formed only on gold electrodes at a sufficiently oxidative potential. This oxidative potential was applied using square-wave pulses, and as expected, the degree of completeness of the monolayers depended upon both the voltage and the period during which it was applied. Using this method, monolayers could be formed quickly, in only twenty 5-s pulses. X-ray photoelectron spectroscopy and infrared spectroscopy supported our hypothesis that this process involves formation of stable gold–thiolate bonds at the gold surface and that (bi)sulfate is a side-product under our experimental conditions. Unlike the preparation of SAMs from alkanethiols, clean gold is not required for forming complete monolayers from alkylthiosulfates. Preliminary results indicate that monolayers of alkanethiols can also be formed by reductive electrolysis of corresponding alkylthiosulfates in aqueous solution.

Introduction

Molecular self-assembly of monolayers (SAMs) provides a simple method to form highly ordered two-dimensional organic assemblies. Among the various systems that display this behavior, the chemisorption of alkanethiols on gold to produce strong gold–thiolate bonds is particularly convenient because of the ease of their preparation.¹ Well-ordered SAMs form spontaneously on gold surfaces within a short period upon immersion of the surface in either a dilute solution or the vapor of an alkanethiol of interest. These monolayers have been used as model systems for fundamental studies of wettability,² adhesion,³

biocompatibility,⁴ and fouling⁵ and have served as the basis for building multilayers⁶ and bio- and analytical sensors,⁷ for immobilizing biomolecules,⁸ and for preparing patterned surfaces.⁹ The very ease of preparation of these SAMs, however, makes their regioselective formation, for example, on only particular features of a pre-existing gold pattern, difficult.

One approach to controlling self-assembly in these systems has focused on the inability of thiolate ions to covalently bind the gold surface directly, without concomitant oxidation.¹⁰ Hence, gold electrodes immersed in a solution of thiolate ions will only adsorb a SAM if held at a sufficiently high potential. Electrochemistry can also be used, though in this case reduction, to remove SAMs

* To whom correspondence should be addressed. Prof. M. S. Freund: Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, R3T 2N2, Canada; fax: 204-474-7608; e-mail: michael_freund@umanitoba.ca. Prof. G. S. Ferguson: Department of Chemistry, Lehigh University, 6 E. Packer Avenue, Bethlehem, PA 18015-3172; fax, 610-758-6536; e-mail, gf03@lehigh.edu.

[†] Department of Chemistry.

[‡] Department of Materials Science & Engineering.

(1) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 448.

(2) Abe, K.; Takiguchi, H.; Tamada, K. *Langmuir* **2000**, *16*, 2394.

Abbott, S.; Ralston, J.; Reynolds, G.; Hayes, R. *Langmuir* **1999**, *15*, 8923. Graupe, M.; Koini, T.; Kim, H. I.; Garg, N.; Miura, Y. F.; Takenaga, M.; Perry, S. S.; Lee, T. R. *Colloids Surf., A* **1999**, *154*, 239. Miura, Y. F.; Takenaga, M.; Koini, T.; Graupe, M.; Garg, N.; Graham, R. L., Jr.; Lee, T. R. *Langmuir* **1998**, *14*, 5821. Engquist, I.; Liedberg, B. *J. Phys. Chem.* **1996**, *100*, 20089. Ulman, A. *Thin Solid Films* **1996**, *273*, 48. Drelich, J.; Miller, J. D.; Good, R. J. *J. Colloid Interface Sci.* **1996**, *179*, 37. Lee, T. R.; Carey, R. I.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 741. Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 1990. Laibinis, P. E.; Fox, M. A.; Folkers, J. P.; Whitesides, G. M. *Langmuir* **1991**, *7*, 3167. Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7164.

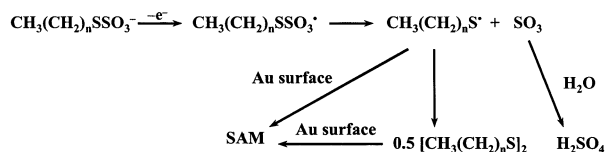
(3) Quon, R. A.; Ulman, A.; Vanderlick, T. K. *Langmuir* **2000**, *16*, 8912. Callow, M. E.; Callow, J. A.; Ista, L. K.; Coleman, S. E.; Nolasco, A. C.; Lopez, G. P. *Appl. Environ. Microbiol.* **2000**, *66*, 3249. Clear, S. C.; Nealey, P. F. *J. Colloid Interface Sci.* **1999**, *213*, 238. Glodde, M.; Hartwig, A.; Hennemann, O.-D.; Stohrer, W.-D. *Int. J. Adhes. Adhes.* **1998**, *18*, 359. Zhuk, A. V.; Evans, A. G.; Hutchinson, J. W.; Whitesides, G. M. *J. Mater. Res.* **1998**, *13*, 3555. Opila, R. L.; Legrange, J. D.; Markham, J. L.; Heyer, G.; Schroeder, C. M. *J. Adhes. Sci. Technol.* **1997**, *11*, 1. Silin, V.; Weetall, H. *Proc. Annu. Meet. Adhes. Soc.* **1996**, *19*, 211. Wienczek, K. M.; Fletcher, M. *J. Bacteriol.* **1995**, *177*, 1959.

(4) Schoenfish, M. H.; Ovadia, M.; Pemberton, J. E. *J. Biomed. Mater. Res.* **2000**, *51*, 209. Bruening, M. L.; Zhou, Y.; Aguilar, G.; Agee, R.; Bergbreiter, D. E.; Crooks, R. M. *Langmuir* **1997**, *13*, 770. Rudolph, A. S. *J. Cell Biochem.* **1994**, *56*, 183.

(5) Retna, R. C.; Ohsaka, T. *Bioelectrochemistry* **2001**, *53*, 251. Grunze, M. *Proc. Annu. Meet. Adhes. Soc.* **2000**, *23*, 4. Wienczek, K. M.; Fletcher, M. *Biofouling* **1997**, *11*, 293. Ista, L. K.; Fan, H.; Baca, O.; Lopez, G. P. *FEMS Microbiol. Lett.* **1996**, *142*, 59. Lindner, E. *Biofouling* **1992**, *6*, 193. Whitesides, G. M.; Ferguson, G. S.; Allara, D.; Scherson, D.; Speaker, L.; Ulman, A. *Rev. Surf. Chem.* **1993**, *3*, 49.

(6) Emberly, E.; Kirczenow, G. *J. Appl. Phys.* **2000**, *88*, 5280. Forzani, E. S.; Solis, V. M.; Calvo, E. *J. Anal. Chem.* **2000**, *72*, 5300. Deng, W.; Fujita, D.; Yang, L.; Nejo, H.; Bai, C. *Jpn. J. Appl. Phys., Part 2* **2000**, *39*, L751. Berlin, A.; Zotti, G. *Macromol. Rapid Commun.* **2000**, *21*, 301. Cheng, Y.; Corn, R. M. *J. Phys. Chem. B* **1999**, *103*, 8726. Nishimura, N.; Ooi, M.; Shimazu, K.; Fujii, H.; Uosaki, K. *J. Electroanal. Chem.* **1999**, *473*, 75. Reinert, W. A.; Jones, L., II; Burgin, T. P.; Zhou, C.-w.; Muller, C. J.; Deshpande, M. R.; Reed, M. A.; Tour, J. M. *Nanotechnology* **1998**, *9*, 246. Nakanishi, T.; Ohtani, B.; Uosaki, K. *J. Phys. Chem. B* **1998**, *102*, 1571. Kaifer, A. E. *Prog. Colloid Polym. Sci.* **1997**, *103*, 193. Clark, S. L.; Montague, M.; Hammond, P. T. *Supramol. Sci.* **1997**, *4*, 141. Lee, Y. J.; Jeon, I. C.; Paik, W.-k.; Kim, K. *Langmuir* **1996**, *12*, 5830. Davis, F.; Stirling, C. J. M. *J. Am. Chem. Soc.* **1995**, *117*, 10385. Tour, J. M.; Jones, L., II; Pearson, D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, S. *J. Am. Chem. Soc.* **1995**, *117*, 9529. Bell, C. M.; Yang, H. C.; Mallouk, T. E. *Adv. Chem. Ser.* **1995**, *245*, 211. Evans, S. D.; Freeman, T. L.; Flynn, T. M.; Batchelder, D. N.; Ulman, A. *Thin Solid Films* **1994**, *244*, 778. Schneider, T. W.; Buttry, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 12391. Spinke, J.; Liley, M.; Guder, H. J.; Angermaier, L.; Knoll, W. *Langmuir* **1993**, *9*, 1821. Thomas, R. C.; Sun, L.; Crooks, R. M.; Ricco, A. J. *Langmuir* **1991**, *7*, 620.

Scheme 1. Proposed Mechanism for the Formation of SAMs by Oxidation of Alkylthiosulfates at a Gold Electrode



that had previously been adsorbed.¹¹ Hence, an alternative strategy for producing patterns involves allowing indiscriminate self-assembly to occur, followed by articulation of a pattern by the selective removal of the SAM from certain electrodes. Cathodic polarization has also been reported to induce the formation of SAMs on selected gold electrodes from alkanethiols, though the mechanism by which this process occurs remains unclear.¹²

In our work, we have focused on an altogether different adsorbate for the formation of SAMs, alkylthiosulfates. Alkylthiosulfates, also known as Bunte salts, can be used to synthesize disulfides by oxidation,¹³ acidic hydrolysis,¹⁴ or alkaline degradation.¹⁵ Disulfides also can be formed from Bunte salts electrochemically.^{16,17} This method has been extended to form polydisulfides from "double" Bunte salts, molecules carrying two thiosulfate groups, using electrochemistry with gold electrodes.¹⁸

At the outset of this work, we hypothesized that if oxidation of Bunte salts occurred at a gold electrode, trapping of the intermediates or products of the oxidation could provide a selective method for driving self-assembly only at electrodes held at a sufficiently high potential. Our hypothesis, summarized in Scheme 1, was that oxidation would lead to formation of an alkylsulfide radical by release of SO₃.^{16,17} This radical could then combine directly with a dangling bond at the gold surface, or could

couple to form disulfide. Either of these pathways would be expected to lead to formation of SAMs, as disulfides readily oxidatively add to gold surfaces.¹⁹ Finally, SO₃ would be expected to react with any water in the solvent to form sulfate (or bisulfate) ions. Sulfuric acid produced in this way could also be involved in monolayer formation, via acid hydrolysis (if the acid were soluble) of the Bunte salt to give thiol.

We recently reported that this approach was successful and provide a more detailed description here.²⁰ Monolayers produced in this way are very similar to those prepared using the conventional adsorption of thiols or disulfides, as indicated by several methods of characterization including contact angle measurements, ellipsometry, and high-resolution X-ray photoelectron spectroscopy (XPS).²⁰ In particular, the XPS results for monolayers produced by both methods were nearly indistinguishable. High-resolution spectra revealed only thiolate photoemission in the sulfur 2p region for both types of SAM, and the measured Au 4f/C 1s ratios were in excellent agreement (differed by less than 10%).²⁰ These results clearly do not support the speculation that THF electropolymerization

(7) Gaspar, S.; Zimmermann, H.; Gazaryan, I.; Csoregi, E.; Schuhmann, W. *Electroanalysis* **2001**, *13*, 284. Ferretti, S.; Paynter, S.; Russell, D. A.; Sapsford, K. E.; Richardson, D. J. *Trends Anal. Chem.* **2000**, *19*, 530. Yang, S.; Perez-Luna, V. H.; Lopez, G. P. *Proc. SPIE-Int. Soc. Opt. Eng.* **2000**, *3926*, 181. Chen, C. S.; Ostumi, E.; Whitesides, G. M.; Ingber, D. E. *Methods Mol. Biol.* **2000**, *139*, 209. Alexander, P. W.; Rechnitz, G. A. *Electroanalysis* **2000**, *12*, 343. Nyquist, R. M.; Eberhardt, A. S.; Silks, L. A., III; Li, Z.; Yang, X.; Swanson, B. I. *Langmuir* **2000**, *16*, 1793. Hseuh, C.-C.; Liu, Y.; Henry, M.; Freund, M. S. *Anal. Chem. Acta* **1999**, *397*, 135. Everhart, D. S. *CHEMTECH* **1999**, *29*, 30. Liedberg, B.; Cooper, J. M. In *Immobilized Biomolecules in Analysis*; Cass, T.; Ligler, F. S., Eds.; Oxford University Press: New York, 1998; pp 55–78. Cotton, C.; Glidle, A.; Beamson, G.; Cooper, J. M. *Langmuir* **1998**, *14*, 5139. Gooding, J. J.; Praig, V.; Hall, E. A. H. *Anal. Chem.* **1998**, *70*, 2396. Chen, C. S.; Mrksich, M.; Huang, S.; Whitesides, G. M.; Ingber, D. E. *Biotechnol. Prog.* **1998**, *14*, 356. Tender, L. M.; Opperman, K. A.; Hampton, P. D.; Lopez, G. P. *Adv. Mater.* **1998**, *10*, 73. Sampath, S.; Lev, O. *Adv. Mater.* **1997**, *9*, 410–413 and references therein.

(8) Collinson, M.; Bowden, E. F.; Tarlov, M. J. *Langmuir* **1992**, *8*, 1247. Willner, I.; Katz, E.; Riklin, R.; Kasher, R. *J. Am. Chem. Soc.* **1992**, *114*, 10967.

(9) Chan, K. C.; Kim, T.; Schoer, J. K.; Crooks, R. M. *J. Am. Chem. Soc.* **1995**, *117*, 5875. Kumar, A.; Whitesides, G. M. *Appl. Phys. Lett.* **1993**, *163*, 2002. Wilber, J. L.; Kim, E.; Xia, Y.; Whitesides, G. M. *Adv. Mater.* **1995**, *7*, 649. Tarlov, M. J.; Burgess, D. R. F., Jr.; Gillen, G. J. *Am. Chem. Soc.* **1993**, *115*, 5305. Gorman, C. B.; Biebuyck, H. A.; Whitesides, G. M. *Chem. Mater.* **1995**, *7*, 526. Gardner, T. J.; Frisbie, C. D.; Wrighton, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 6927. Tao, Y.-T.; Kannaiyan, P.; Lee, W.-C. *Langmuir* **1998**, *14*, 6158. Xia, Y.; Zhou, X.-M.; Whitesides, G. M. *Microelectron. Eng.* **1996**, *32*, 255. Wilbur, J. L.; Biebuyck, H. A.; MacDonald, J. C.; Whitesides, G. M. *Langmuir* **1995**, *11*, 827. Bar, G.; Rubin, S.; Parikh, A. N.; Swanson, B. I.; Zawodzinski, T. A.; Whangbo, M. H. *Langmuir* **1997**, *13*, 373. Bar, G.; Rubin, S.; Taylor, T. N.; Swanson, B. I.; Zawodzinski, T. A.; Chow, J. T.; Ferraris, J. P. *J. Vac. Sci. Technol., A* **1996**, *14*, 1794. Hayes, W. A.; Kim, H.; Yue, X.; Perry, S. S.; Shannon, C. *Langmuir* **1997**, *13*, 2511.

(10) Weisshaar, D. E.; Lamp, B. D.; Porter, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 5860. Tender, L. M.; Worley, H.; Fan, H.; Lopez, G. P. *Langmuir* **1996**, *12*, 5515. Riepl, M.; Mirsky, V. M.; Wolfbeis, O. S. *Mikrochim. Acta* **1999**, *131*, 29. Applied positive potentials also accelerate the adsorption of SAMs from alkanethiols in ethanol. See: Ron, H.; Rubinstein, I. *J. Am. Chem. Soc.* **1998**, *120*, 13444.

(11) Widrig, C. A.; Chung, C.; Porter, M. D. *J. Electroanal. Chem.* **1991**, *310*, 335. Walczak, M. M.; Popenoe, D. D.; Deihammer, R. S.; Lamp, B. D.; Chung, C.; Porter, M. D. *Langmuir* **1991**, *7*, 2687. Walczak, C. A.; Alves, C. A.; Lamp, B. D. *J. Electroanal. Chem.* **1995**, *396*, 103. Zhong, C.-J.; Porter, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 11616. Hobara, D.; Ota, M.; Imabayashi, S.-i.; Niki, K.; Kakiuchi, T. *J. Electroanal. Chem.* **1998**, *444*, 113. Nishizawa, M.; Sunagawa, T.; Yoneyama, H.; Suita, Y.-o. *J. Electroanal. Chem.* **1997**, *436*, 213. Wittstock, R.; Hesse, R.; Schuhmann, W. *Electroanalysis* **1997**, *9*, 746. Tender, L. M.; Opperman, K. A.; Hampton, P. D.; Lopez, G. P. *Adv. Mater.* **1998**, *10*, 73. Imabayashi, S.-i.; Hobara, D.; Kakiuchi, T. *Langmuir* **2001**, *17*, 2560. Sawaguchi, T.; Sato, Y.; Mizutani, F. *J. Electroanal. Chem.* **2001**, *496*, 50. Kakiuchi, T.; Iida, M.; Gon, N.; Hobara, D.; Imabayashi, S.-i.; Niki, K. *Langmuir* **2001**, *17*, 1599. Esplandi, M. J.; Hagenstroem, H.; Kolb, D. M. *Langmuir* **2001**, *17*, 828. Kawaguchi, T.; Yasuda, H.; Shimazu, K.; Porter, M. D. *Langmuir* **2000**, *16*, 9830. Kakiuchi, T.; Sato, K.; Iida, M.; Hobara, D.; Imabayashi, S.-i.; Niki, K. *Langmuir* **2000**, *16*, 7238. Wong, S.-S.; Porter, M. D. *J. Electroanal. Chem.* **2000**, *485*, 135. Hobara, D.; Ueda, K.; Imabayashi, S.-i.; Yamamoto, M.; Kakiuchi, T. *Electrochemistry* **1999**, *67*, 1218. Byloos, M.; Al-Maznai, H.; Morin, M. *J. Phys. Chem. B* **1999**, *103*, 6554. Kondo, T.; Yanagida, M.; Shimazu, K.; Uosaki, K. *Langmuir* **1998**, *14*, 5656. Aoki, K.; Kakiuchi, T. *J. Electroanal. Chem.* **1998**, *452*, 187. Hobara, D.; Miyake, K.; Imabayashi, S.-i.; Niki, K.; Kakiuchi, T. *Langmuir* **1998**, *14*, 3590. Szafrański, C. A.; Tanner, W.; Laibinis, P. E.; Garrell, R. L. *Langmuir* **1998**, *14*, 3570. Yang, D.-F.; Morin, M. *J. Electroanal. Chem.* **1998**, *441*, 173. Sato, Y.; Mizutani, F.; Tsukuba, H. *J. Electroanal. Chem.* **1997**, *438*, 99. Arnold, S.; Feng, Z. Q.; Kakiuchi, T.; Knoll, W.; Niki, K. *J. Electroanal. Chem.* **1997**, *438*, 91. Imabayashi, S.-i.; Hobara, D.; Kakiuchi, T.; Knoll, W. *Langmuir* **1997**, *13*, 4502. Yang, D.-F.; Morin, M. *J. Electroanal. Chem.* **1997**, *429*, 1. Imabayashi, S.-i.; Iida, M.; Hobara, D.; Feng, Z. Q.; Niki, K.; Kakiuchi, T. *J. Electroanal. Chem.* **1997**, *428*, 33. Zhong, C.-J.; Zak, J.; Porter, M. D. *J. Electroanal. Chem.* **1997**, *421*, 9. Yang, D.-F.; Al-Maznai, H.; Morin, M. *J. Phys. Chem. B* **1997**, *101*, 1158. Yang, D.-F.; Wilde, C. P.; Morin, M. *Langmuir* **1997**, *13*, 243. McCarley, T. D.; McCarley, R. L. *Anal. Chem.* **1997**, *69*, 130. Kwan, W. S. V.; Penneau, J. F.; Miller, L. L. *J. Electroanal. Chem. Interfacial Electrochem.* **1990**, *291*, 295.

(12) Wang, J.; Jiang, M.; Kawde, A. M.; Polsky, R. *Langmuir* **2000**, *16*, 9687.

(13) Affleck, J. G.; Dougherty, G. *J. Org. Chem.* **1950**, *15*, 865. Milligan, B. L.; Swan, L. M. *J. Chem. Soc.* **1962**, 2172.

(14) Bunte, H. *Chem. Ber.* **1874**, *7*, 646. Westlake, H. E., Jr.; Dougherty, G. *J. Am. Chem. Soc.* **1941**, *63*, 658. Weiss, U.; Sokol, A. *J. Am. Chem. Soc.* **1942**, *64*, 149. Weiss, U.; Sokol, A. *J. Am. Chem. Soc.* **1950**, *72*, 1687. Distler, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 544. Kice, J. L. *J. Org. Chem.* **1963**, *28*, 957.

(15) Alonso, M. E.; Aragona, H. *Org. Synth.* **1978**, *58*, 147. Price, T. S.; Twiss, D. F. *J. Chem. Soc.* **1908**, 1395. Price, T. S.; Twiss, D. F. *J. Chem. Soc.* **1908**, 1401.

(16) Price, T. S.; Twiss, D. F. *J. Chem. Soc.* **1907**, 2021.

(17) Czerwinski, A.; Orzeszko, A.; Kazimierczuk, Z.; Marassi, R.; Zamponi, S. *Anal. Lett.* **1997**, *30*, 2391.

(18) Orzeszko, A.; Czerwinski, A.; Kazimierczuk, Z. *J. Polym. Mater.* **1997**, *11*, 21. Orzeszko, A. *J. Polym. Mater.* **1994**, *11*, 69.

(19) Ulman, A. *An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly*; Academic Press: New York, 1991.

(20) Lee, M.-T.; Hsueh, C.-C.; Freund, M. S.; Ferguson, G. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1228.

is the source of the observed surface passivation under our conditions.²¹ A focus of the present study was to address aspects of the mechanism of the electrochemical synthesis of monolayers in this way, including the inhibition of spontaneous chemisorption of alkylthiosulfates in the presence of tetrabutylammonium tetrafluoroborate, and identification of the side-product(s) of the process. In addition, we describe the formation of SAMs of alkanethiolates by reduction of Bunte salts in aqueous solution.

Experimental Section

General. Hexadecanethiol (Aldrich, 92%) was purified by distillation under vacuum prior to use. Tetrabutylammonium tetrafluoroborate, tetrabutylammonium hexafluorophosphate (98%), tetrabutylammonium perchlorate (99%), lithium perchlorate (95+%), sodium hydrogen sulfate (technical grade), 1-bromohexadecane (97%), 1-bromotetradecane (97%), 1-bromododecane (96%), 1-bromooctane (98%), 1-bromooctane (99%), potassium ferricyanide (99%), potassium ferrocyanide (99%), and sodium thiosulfate pentahydrate (99.5%) were obtained from Aldrich and used as received. Dicyclopentadienyliron (98%) was obtained from Alfa and used as received. Absolute ethanol (McCormick Distilling Co.), sodium sulfate (EM Science, 99%), and silver nitrate (Kodak, 99.9%) were used as received. The hexadecane (Aldrich, 99%) used in the contact-angle measurements was purified by percolation twice through activated alumina. Tetrahydrofuran (THF; EM science, 99.94%) was distilled from sodium-benzophenone ketyl before use. Gold (99.99%) was obtained from the Refining System Co. and used as received. Pump oil used in the "dirty gold" experiment was from VWR Scientific (vacuum pump oil no. 19) and was used as received. All water used in this work was purified with a Millipore Milli-Q system to a resistivity of at least 15 M Ω ·cm. ¹H NMR spectra were acquired using a Bruker AMX 360 spectrometer, referenced to CHCl₃ at 7.24 ppm, and are reported in units of δ . Infrared spectra were collected using a Perkin-Elmer FT-IR 1600 spectrometer, at a resolution of 2 cm⁻¹. In each case, 64 scans were averaged to achieve a satisfactory signal-to-noise ratio.

Preparation of Sodium Alkylthiosulfates, CH₃(CH₂)_n-S₂O₃Na (n = 7, 9, 11, 13, 15). The Bunte salts were prepared following a literature procedure.¹⁴ For example, 1-bromohexadecane (1.53 g, 5 mmol) dissolved in 20 mL of ethanol was added to a solution of sodium thiosulfate (1.24 g, 5 mmol) in 20 mL of water, and the mixture was brought to reflux until the solution became homogeneous. The solution was then cooled to room temperature, allowing the hexadecylthiosulfate to precipitate. The white solid was filtered and recrystallized using ethanol. ¹H NMR: CH₃(CH₂)₁₅SSO₃Na, 0.86 (t, 3H); CH₃(CH₂)₁₃CH₂CH₂SSO₃Na, 1.31–1.50 (m, 26H); CH₃(CH₂)₁₁CH₂CH₂SSO₃Na, 1.65 (m, 2H); CH₃(CH₂)₉CH₂CH₂SSO₃Na, 2.66 (t, 2H).

Preparation of Gold Substrates. Preparation of the glass microscope slides used as working electrodes has been described elsewhere.²⁰ Briefly, treatment by (3-mercaptopropyl)trimethoxysilane enhanced the adhesion between the gold overlayer and the glass slides. Gold films with a final thickness of 1000 Å were deposited by thermal evaporation at ~0.5 Å/s at a background pressure of ~2 × 10⁻⁶ Torr.

Electrochemistry. The electrochemical experiments were conducted using a Bioanalytical Systems BAS-100B or an EG&G potentiostat/galvanostat model 273 from Princeton Applied Research. A conventional three-electrode configuration was employed, with gold-coated glass as the working electrode. The counter electrode was a platinum flag (7 mm × 20 mm). A glass tube with a Vycor tip containing Ag/AgNO₃ (3 mM)²² with 0.1 M Bu₄NBF₄ as a supporting electrolyte, in acetonitrile was used as the reference electrode. The potential of the reference electrode was verified against ferrocene–ferricinium as a probe redox couple prior to these experiments. All the cyclic voltammograms reported in this paper started with a scan in the anodic direction

from -0.90 V and were collected at 100 mV/s in the presence of 0.1 M Bu₄NBF₄ as a supporting electrolyte.

Monolayers were formed using square-wave potentiometric pulses. For example, a gold electrode was placed into 20 mL of a 10 mM sodium hexadecylthiosulfate solution with 0.10 M Bu₄NBF₄ in THF. The potential was stepped from -0.90 to 1.20 V, held at 1.20 V for 5 s, and then stepped back to the -0.90 V resting potential. After 5 potentiometric pulses, the sample was rinsed with THF, ethanol, and water and then dried with a stream of N₂.

X-ray Photoelectron Spectroscopy. The XPS spectra in this paper were obtained using a Scienta ESCA-300 spectrometer, equipped with a rotating anode (Al K α) source producing approximately 39.0 kW of X-ray power, a monochromator, and a 300-mm (diameter) hemispherical analyzer. All spectra were collected at a 20° takeoff angle between the plane of the surface and the detector, using a slit width of 11 mm, and were referenced to the Au 4f_{7/2} peak set at 84.0 eV. The background pressure in the sample chamber was 2 × 10⁻⁹ Torr. Survey scans were collected with a pass energy of 75 eV and a step energy of 1.0 eV and took 5.5 min to complete. Sulfur 2p regional scans were collected with a pass energy of 150 eV and a step energy of 0.05 eV and took 10 min to complete (5 scans). Carbon 1s regional scans were collected with a pass energy of 150 eV and a step energy of 0.05 eV and took 4.5 min to complete (2 scans). Gold 4f_{7/2} regional scans were collected with a pass energy of 75 eV and a step energy of 0.2 eV and took 1 min to complete (single scan). Oxygen 1s regional scans were collected with a pass energy of 150 eV and a step energy of 0.05 eV and took 6 min to complete (3 scans). Sodium 1s regional scans were collected with a pass energy of 150 eV and a step energy of 0.05 eV and took 6.5 min to complete (5 scans).

For quantitative analysis, the sensitivity factors used to correct the number of counts under each peak (or envelope) were as follows: Au 4f_{7/2}, 9.58; C 1s, 1.000; O 1s, 2.8370; S 2p (both components), 2.1735; and Na 1s, 8.520. The sensitivity factors for oxygen, carbon, sulfur, and sodium photoemission were determined by A. C. Miller with the Scienta ESCA-300 at Lehigh University. The value for gold is the Scofield value.²³ The curve fitting was performed using Scienta ESCA system software²⁴ following a published procedure.²⁵ Each peak was described as a sum of Gaussian and Lorentzian functions, assuming a linear baseline. For C 1s photoemission, all fits had reasonable mixing ($m \geq 0.85$) and asymmetry ($A \leq 0.12$) ratios, as well as acceptable line widths (1.00–1.25 eV, full width at half-maximum (fwhm)). For Au 4f_{7/2} photoemission, all fits had reasonable mixing ($m \geq 0.70$) and asymmetry ($A \leq 0.14$) ratios, with line widths between 0.65 and 0.68 eV (fwhm). For S 1s photoemission, all fits had reasonable mixing ($m \geq 0.60$) and asymmetry ($A \leq 0.21$) ratios, as well as acceptable line widths (0.60–0.860 eV, fwhm). For Na 1s photoemission, the fwhm was 1.79 eV, with reasonable asymmetry mixing ($m = 1$) and asymmetry ($A = 0.012$) ratios. For O 1s photoemission, the fwhm was 1.39 eV, with reasonable mixing ($m = 1$) and asymmetry ($A = 0.14$) ratios.

Contact-Angle and Ellipsometric 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. Ellipsometric measurements were made using an automatic null ellipsometer (Rudolph Auto-EL III) with a helium–neon laser ($\lambda = 632.8$ nm) set at an incident angle of 70°. Measurements were taken at three spots on the samples. Film thickness was determined using the manufacturer's program, assuming a refractive index of the monolayer of 1.5.

Quartz Crystal Microbalance (QCM) Measurements. QCM measurements were performed using an EG&G QCA 197 microbalance analyzer coupled to an EG&G 273A potentiostat/galvanostat. The quartz crystals were AT-cut (EG&G) with a resonant frequency of 10 MHz. The active portions of the quartz were coated with Au and had an active area of 0.20 cm² and a sensitivity of 1.96 ± 0.07 ng/Hz, determined by the electro-

(23) Scofield, J. H. *J. Electron. Spectrosc.* **1976**, *8*, 129.

(24) *Scienta ESCA300 Users' Manual*; Scienta: Uppsala, Sweden, 1997.

(25) Beamson, G.; Briggs, D. *High-Resolution XPS of Organic Polymers*; The Scienta ESCA300 Database; Wiley: New York, 1992.

(21) Nann, T.; Urban, G. A. *J. Electroanal. Chem.* **2001**, *505*, 125.

(22) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; John Wiley & Sons: New York, 1980; p 53.

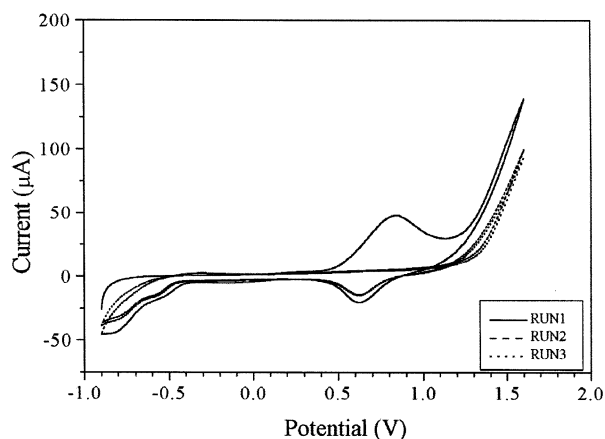


Figure 1. Cyclic voltammograms for a 10 mM solution of sodium *n*-hexadecylthiosulfate in THF from -0.90 to 1.60 V (0.1 M LiClO_4 , 100 mV/s) using a gold working electrode and a Ag/AgNO_3 reference electrode (3 mM in CH_3CN).

chemical deposition of copper. The scan rate in all of the experiments using the QCM was 10 mV/s. The solutions in these experiments contained 10 mM hexadecylthiosulfate in THF with 0.1 M Bu_4NBF_4 as a supporting electrolyte.

Results and Discussion

Oxidation of Alkylthiosulfates. Alkylthiosulfates, $\text{CH}_3(\text{CH}_2)_n\text{S}_2\text{O}_3\text{Na}$ ($n = 7, 9, 11, 13,$ and 15), were synthesized by nucleophilic displacement reactions between sodium thiosulfate and the corresponding alkyl bromides and purified by recrystallization in ethanol, according to a reported procedure.¹⁴ Our initial studies of the electrochemistry of these alkylthiosulfates were carried out using cyclic voltammetry in various solvents, for example, acetonitrile, water, ethanol, and ethanol/water (50:50), but the oxidation was only observed in THF. Different supporting electrolytes were also used, with widely varying results. For example, the cyclic voltammogram (-0.90 to 1.60 V) of hexadecylthiosulfate in THF using LiClO_4 as the supporting electrolyte contained an oxidation peak at 0.95 V in the first anodic scan, which then decreased significantly in the following scans (Figure 1). The sample became more hydrophobic after 2 cyclic scans, but an ordered monolayer did not form: contact angles of hexadecane on the surface after even 200 scans (16 – 18°) indicated that the monolayer was incomplete. The cathodic wave present in the first two scans was presumably associated with reduction of gold oxide, which was not produced when a partial SAM was present (third scan). Cycling to a lower potential (1.2 V) avoided this problem and produced a nearly complete monolayer with contact angles of hexadecane of 42 – 44° (Figure 2). Control experiments, however, suggested that formation of this monolayer could have been due primarily to spontaneous chemisorption rather than to the electrochemical process (*vide infra*). Cycling to the low positive potential in these experiments apparently avoided the oxidative desorption found at potentials approaching ~ 1.60 V.

In contrast, the voltammogram of hexadecylthiosulfate in THF with 0.1 M Bu_4NBF_4 as the supporting electrolyte contained an oxidation peak in the first anodic scan, which decreased only gradually in subsequent scans (Figure 3). The current rose sharply and reached a maximum at approximately 0.95 V before decreasing again, consistent with a decrease in the concentration of the Bunte salt near the gold electrode or blocking of the electrode by the resulting monolayer at the gold surface. The peak current due to oxidation of the Bunte salt gradually decreased in

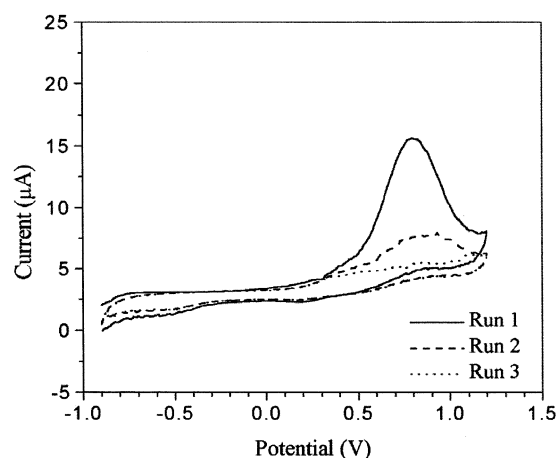


Figure 2. Cyclic voltammograms for a 10 mM solution of sodium *n*-hexadecylthiosulfate in THF from -0.90 to 1.20 V (0.1 M LiClO_4 , 100 mV/s) using a gold working electrode and a Ag/AgNO_3 reference electrode (3 mM in CH_3CN).

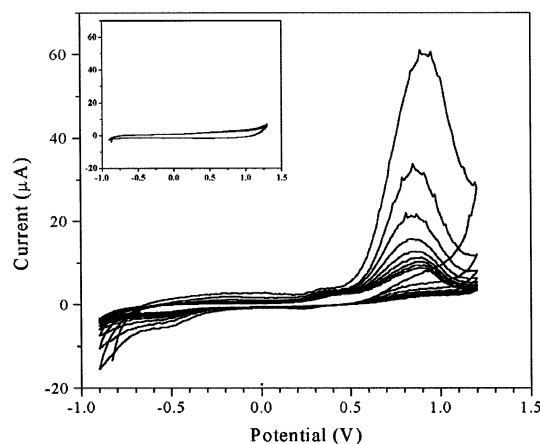


Figure 3. Cyclic voltammograms for a 10 mM solution of sodium *n*-hexadecylthiosulfate in THF (0.1 M Bu_4NBF_4 , 100 mV/s) using a gold working electrode and a Ag/AgNO_3 reference electrode (3 mM in CH_3CN). The inset plot shows a cyclic voltammogram for a bare gold electrode in THF (0.1 M Bu_4NBF_4 , 100 mV/s) using a Ag/AgNO_3 reference electrode.

each successive scan until about the sixth scan, after which it remained unchanged. This decrease in current in each successive scan was likely due to the decrease of free gold surface after each scan, arising from chemisorption of the SAM.

Electrochemical Formation of Ordered Monolayers. As with LiClO_4 , cycling to 1.60 V with Bu_4NBF_4 as the supporting electrolyte did *not* produce ordered SAMs. A monolayer formed in this way, using even 200 scans, had a contact angle of hexadecane of only 30° . For comparison, monolayers formed by chemisorption of hexadecanethiol gave contact angles of hexadecane of 44 – 46° . Cycling to a lower potential (from -0.90 to 1.20 V or -0.90 to 1.30 V) for 8 scans, however, did produce ordered monolayers with contact angles of hexadecane of 45 – 46° .

To simplify the process, we explored the use of potentiometric "pulses" to assess our ability to form SAMs electrochemically. In these experiments, a gold electrode was immersed into a solution (THF, 0.1 M Bu_4NBF_4) of an alkylthiosulfate, for example, sodium *n*-tetradecylthiosulfate, and the potential was stepped from a resting value of -0.90 V (vs Ag/AgNO_3) to a particular value in the range producing anodic current in the cyclic voltammogram. The gold electrode was held at this potential for 5 s and then stepped back to the -0.90 V resting

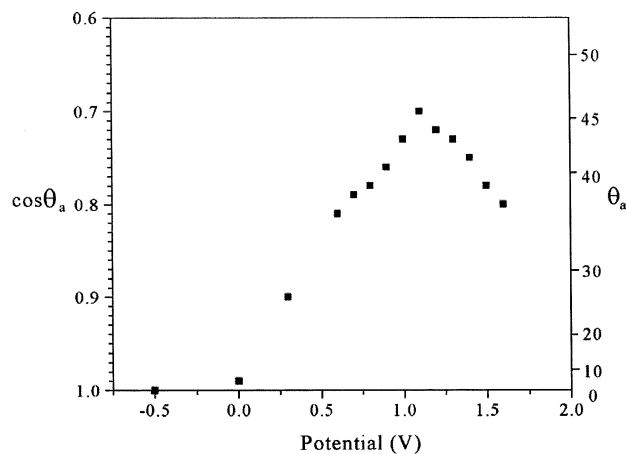


Figure 4. Advancing contact angles of hexadecane on SAMs formed by electrochemical oxidation of tetradecylthiosulfate using five voltametric pulses to different potentials.

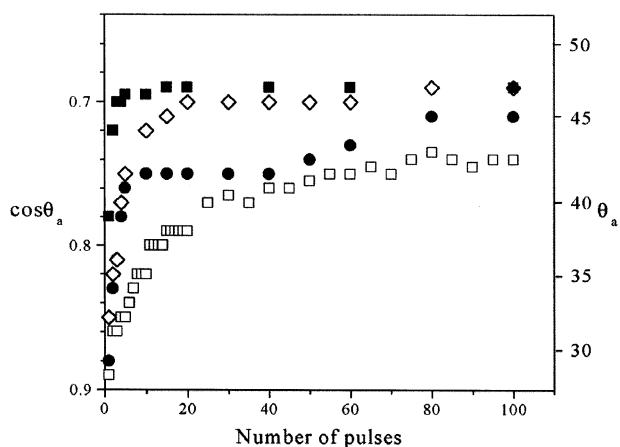


Figure 5. Advancing contact angles of hexadecane on SAMs formed by electrochemical oxidation of tetradecylthiosulfate as a function of the number of voltametric pulses using the potentials to 0.90 (●), 1.00 (◇), 1.10 (■), or 1.60 (□) V.

potential for 5 s. To optimize the procedure for synthesizing SAMs, this process was repeated 5 times using a separate sample for each potential from -0.50 to 1.60 V in 0.1 -V increments. The degree of completeness of each resulting monolayer was assessed by measuring the advancing contact angles of hexadecane on its surface as shown in Figure 4. The contact angles increased with increasing applied potential, up to about 1.10 V, above which the contact angles began to decrease. The maximum contact angles (45 – 46°) agreed with those reported for complete, well-ordered SAMs prepared by the chemisorption of tetradecanethiol (44 – 46°).²⁶

We also followed the growth of these films systematically, as a function of the number of potentiometric pulses to a given potential, by monitoring wettability by hexadecane on monolayers formed by electrolysis of tetradecylthiosulfate. Figure 5 shows these data for SAMs generated with from 1 to 100 pulses to 0.90 , 1.00 , 1.10 , and 1.60 V. Using 0.90 V as the working potential, the contact angles of hexadecane on gold rose from 0 to 42° in the first 10 pulses and then increased slowly to 45° after 100 cycles. With 1.00 V as the working potential, the contact angles of hexadecane reached 44° after 10 pulses and leveled off at 46° after 20 pulses. The optimum working potential for tetradecylthiosulfates, however, was 1.10 V,

(26) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321.

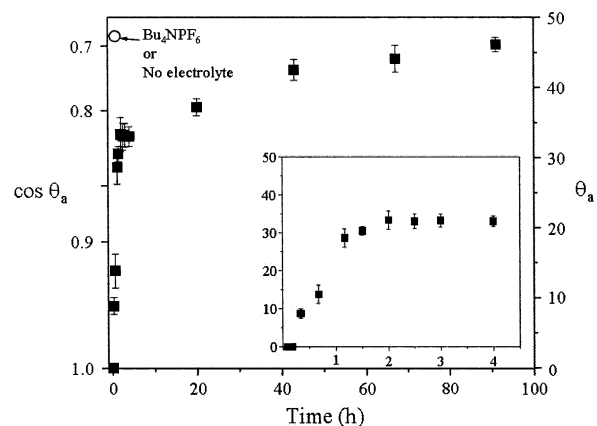


Figure 6. Advancing contact angles of hexadecane (θ_a) on a gold electrode as a function of the immersion time in a 10 mM solution of sodium *n*-hexadecylthiosulfate with (■) and without (○) 0.1 M Bu_4NBF_4 . The inset plot shows the change of contact angles of hexadecane during the first 4 h.

giving a SAM with a hexadecane contact angle of 44° after only 3 pulses, quickly leveling off at 46° after only 5 cycles. Consistent with our results from cyclic voltammetry, using potentials higher than this optimum value gave incomplete monolayers. For example, pulses to 1.60 V gave lower contact angles of hexadecane in the first 20 pulses and did not produce a monolayer with satisfactory contact angles after even 100 pulses.

The data in Figures 4 and 5 are consistent with ion migration and/or electron tunneling being important as these SAMs approach completion and explain why more complete SAMs are formed at higher potentials, up to the point where degradative oxidation becomes a problem.²⁷ At a partially completed SAM, a potential slightly lower than the optimum potential, that is, 1.00 versus 1.10 V, may not provide enough energy for an alkylthiosulfate ion to migrate, or for an electron to tunnel, through the film. Therefore, many more pulses were needed at 1.00 V than at 1.10 V to get complete coverage. At an even lower potential (e.g., 0.90 V), the monolayer only approached but did not reach completion. Potentials higher than 1.10 V resulted in oxidation of the gold, the SAM, or the solvent, with concomitant disordering of the monolayer. The optimum potential to produce complete SAMs, judged by contact angles of hexadecane, varied as a function of the length of the alkyl chain of the alkylthiosulfates. We formed high-quality SAMs from dodecylthiosulfates at 1.00 V and from hexadecylthiosulfate at 1.20 V. The increase in potential necessary for formation of complete monolayers with increasing alkyl chain length is consistent with our hypotheses that ion migration and/or electron tunneling became important as these SAMs approached completion.

In the absence of Bu_4NBF_4 , a solution of hexadecylthiosulfate (10 mM in THF) formed a complete monolayer on gold spontaneously within 15 min, consistent with related observations by Lukkari and co-workers.²⁸ Thus, the selectivity of our approach depends on the ability of Bu_4NBF_4 to inhibit this spontaneous process in THF. In the presence of 0.1 M Bu_4NBF_4 , it took 91 h to form an ordered monolayer by the spontaneous chemisorption of hexadecylthiosulfates in THF (Figure 6). Table 1 shows the contact angles of hexadecane on gold surfaces after treatment with THF solutions of hexadecylthiosulfate for

(27) Miller, C.; Curndet, P.; Grätzel, M. *J. Phys. Chem.* **1991**, *95*, 877.

(28) Lukkari, J.; Meretoja, M.; Kartio, I.; Laajalehto, K.; Rajamaeki, M.; Lindstroem, M.; Kankare, J. *Langmuir* **1994**, *10*, 3529.

Table 1. Contact Angles of Hexadecane on SAMs Formed by Spontaneous Chemisorption of Hexadecylthiosulfate after 15 min in the Presence/Absence of Tetrabutylammonium Tetrafluoroborate

θ_a (deg)	[Bu ₄ NBF ₄]/[C ₁₆ H ₃₃ S ₂ O ₃ Na]			
	0	1	5	10
	46	42	16	<10

15 min in the presence of various amounts of Bu₄NBF₄. As expected, low concentrations of Bu₄NBF₄ allowed monolayer formation to proceed to near completion within this time period, whereas higher concentrations significantly inhibited growth. Chemisorption was not inhibited, however, when tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) or tetrabutylammonium perchlorate (Bu₄NClO₄) was used as the supporting electrolyte instead of Bu₄NBF₄, indicating that the tetrafluoroborate anion is responsible for inhibition of spontaneous chemisorption. One possible explanation may be the basicity of tetrafluoroborate in nonaqueous solvents such as THF, which could prevent acid hydrolysis of the Bunte salt to produce thiol. In contrast to its effect on the chemisorption of alkylthiosulfates, the presence of Bu₄NBF₄ (0.1 M in THF) did not appear to inhibit the formation of SAMs from hexadecanethiol (10 mM).

When using platinum or graphite instead of gold as the working electrode (THF, 0.1 M Bu₄NBF₄), we did not observe oxidation attributable to the Bunte salt by cyclic voltammetry between -0.90 and 1.20 V. Figure 7 shows typical voltammograms for hexadecylthiosulfate (10 mM in THF, 0.1 M Bu₄NBF₄) using graphite and platinum as the working electrode, respectively. To rule out the possibility of electrode fouling during the cyclic scans, the electrodes were checked using ferrocene–ferricinium as a probe redox couple. Both electrodes showed normal electrochemical responses both before and after the Bunte salt experiments (Figure 7, inset plots). Interestingly, the bulk electrolysis of Bunte salts at platinum electrodes in acidic water (0.1 M H₂SO₄ or 0.5 M NaHSO₄) has been reported previously.¹⁷ Our results clearly indicate the involvement of gold surface chemistry in the electrochemically directed self-assembly of Bunte salts to form monolayers.

Mechanism of Monolayer Formation by Electrolysis. Our mechanistic hypothesis, summarized in Scheme 1, for the formation of SAMs in this way proposes the loss of SO₃ from the initially formed radical, followed by hydration to produce sulfuric acid. Because sulfate salts of sodium are only sparingly soluble in THF, one might expect precipitation at the electrode surface. To test this hypothesis, we used X-ray photoelectron spectroscopy to analyze monolayers formed by oxidation of hexadecylthiosulfate, both before and after rinsing with water. The monolayers used in these studies were formed by electrolysis at 1.20 V using 5 pulses. Monolayers were formed on two samples, after which one sample was rinsed with dry THF and the other was rinsed with dry THF and then with water. The survey spectra (Figure 8) of these two samples were similar, except for the photoemission due to Na (1s) at 1072.0 eV and O (1s) at 532.5 eV in the sample rinsed only with THF. The surface ratio of sodium/sulfur/oxygen was 1.5:1:4, based on high-resolution spectra, indicating a mixture of bisulfate and sulfate was produced during the electrolysis.²⁹ To minimize the influence of damage to the sample, these high-resolution spectra were collected from a different spot on the sample

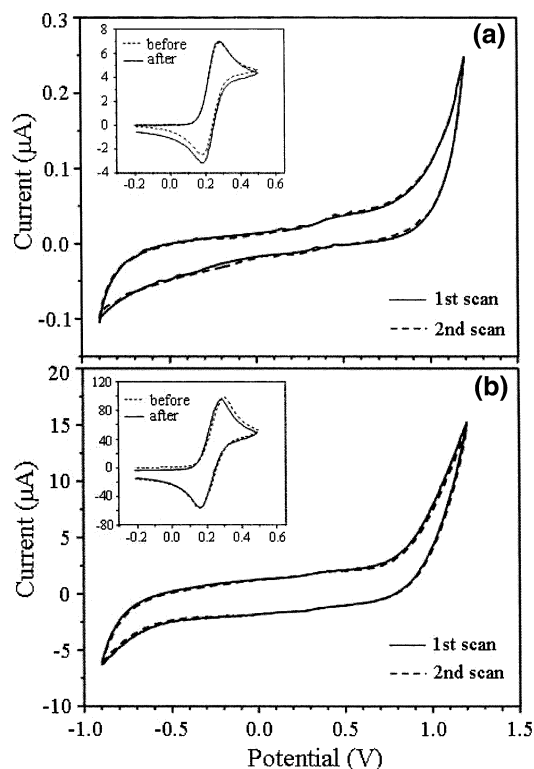


Figure 7. (a) Cyclic voltammograms for a 10 mM solution of sodium *n*-hexadecylthiosulfate in THF (0.1 M Bu₄NBF₄, 100 mV/s) using a graphite working electrode and a Ag/AgNO₃ reference electrode (3 mM in CH₃CN). The inset plot shows a cyclic voltammogram for a graphite electrode in a solution of 10 mM ferrocene before and after the cyclic voltammetry. (b) Cyclic voltammograms for a 10 mM solution of sodium *n*-hexadecylthiosulfate in THF (0.1 M Bu₄NBF₄, 100 mV/s) using a platinum working electrode and a Ag/AgNO₃ reference electrode (3 mM in CH₃CN). The inset plot shows a cyclic voltammogram for a platinum electrode in a solution of 10 mM ferrocene before and after the cyclic voltammetry.

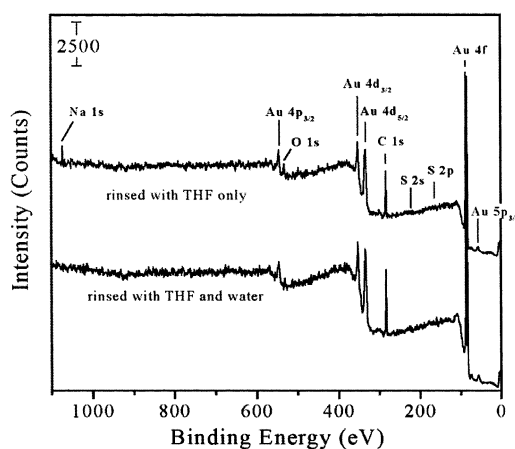


Figure 8. X-ray photoelectron survey spectra of SAMs formed by electrochemisorption of hexadecylthiosulfate and washed with only THF or washed with THF and water.

from where the survey spectrum and other regional scans (Au, C, and S 2p duplicate) were obtained. The sulfur spectrum was collected twice so that this ratio came from the same spot as the oxygen and sodium.

(29) Audi, A. A.; Sherwood, P. M. A. *Surf. Interface Anal.* **2000**, *29*, 265. Olsson, C.-O. A.; Agarwal, P.; Frey, M.; Landolt, D. *Corros. Sci.* **2000**, *42*, 1197. Ardizzone, S.; Bianchi, C. L. *Appl. Surf. Sci.* **1999**, *152*, 63. Engström, P.; Amernstsson, A.; Skoglundh, M.; Fridell, E.; Smedler, G. *Appl. Catal., B* **1999**, *22*, 35.

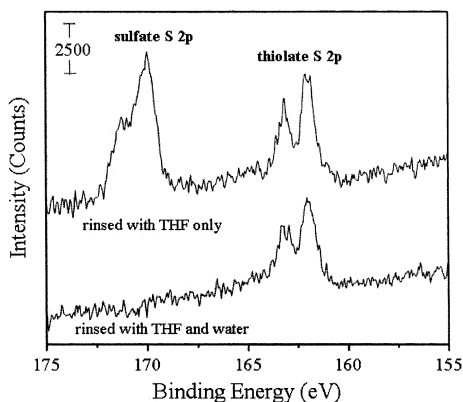


Figure 9. High-resolution sulfur 2p X-ray photoelectron spectra of SAMs formed by electrochemisorption of hexadecylthiosulfate and washed with only THF or washed with THF and water.

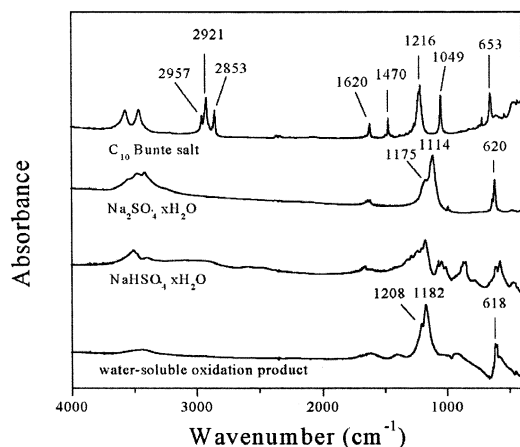


Figure 10. The infrared spectra of (from the bottom) the water-soluble portion of the product of bulk electrolysis of sodium hexadecylthiosulfate in THF, sodium bisulfate, sodium sulfate, and sodium *n*-decylthiosulfatete.

High-resolution scans in the sulfur 2p region (Figure 9) revealed an additional difference: the sample rinsed only with THF contained two types of sulfur, a spin-orbit doublet at 162.0 and 163.1 eV due to the thiolate and an additional doublet at higher binding energy (170.0 and 171.3 eV) assigned to sulfate.²⁹ In contrast, the monolayer washed with THF and water contained photoemission from sulfur only as thiolate (162.0 and 163.2 eV). These data are consistent with the proposed conversion of alkylthiosulfate to thiolate and sulfate, as summarized in Scheme 1.

Because sulfate is produced stoichiometrically in Scheme 1, we expected bulk electrolysis of hexadecylthiosulfate to produce a large amount of it. Indeed, 72 h of continuous pulses to 1.20 V were applied in 20 mL of a 30 mM hexadecylthiosulfate solution (0.3 M Bu₄NBF₄) in THF at a gold electrode. A white solid precipitated onto the electrode during the electrolysis. The solution was centrifuged and the precipitate collected, and an infrared spectrum of the crude solid indicated the presence of a mixture of Bu₄NBF₄, Na₂SO₄, and NaHSO₄. After extraction of the Bu₄NBF₄ with THF, the infrared spectrum of the purified solid (Figure 10) indicated that the product was mainly NaHSO₄.³⁰

(30) For an infrared spectrum of NaHSO₄, see: Baran, J.; Ilcyszyn, M. M.; Marchewka, M. K.; Ratajczak, H. *Spectrosc. Lett.* **1999**, *32*, 83. For infrared spectra of Na₂SO₄, see: Davies, J. E. D.; Sandford, W. F. *J. Chem. Soc., Dalton Trans.* **1975**, *19*, 1912. Durie, R. A.; Milne, J. W. *Spectrochim. Acta, Part A* **1978**, *34A*, 215.

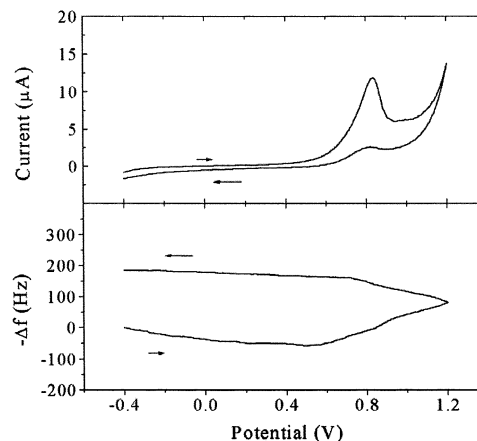


Figure 11. Cyclic voltammogram and corresponding QCM frequency change for a 10 mM solution of sodium *n*-hexadecylthiosulfate in THF (0.1 M Bu₄NBF₄, 10 mV/s) using a gold QCM working electrode and a Ag/AgNO₃ reference electrode (3 mM in CH₃CN).

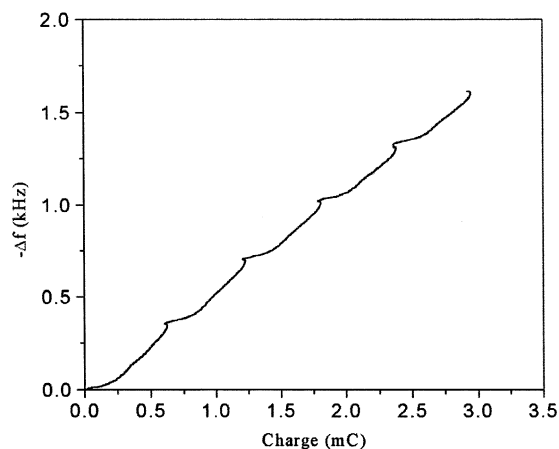


Figure 12. Plot of frequency change versus charge passed during repetitive cycling of a gold QCM working electrode under the same conditions as those described in Figure 11. These QCM measurements were made after the anodic peak in successive voltametric scans had decreased to a nearly constant level (see Figure 3).

In situ QCM measurements further demonstrated the formation of insoluble sulfate as a side-product during the electrolysis. Figure 11 shows a cyclic voltammogram and the corresponding increase in mass (decrease in frequency) at a gold electrode on an oscillating QCM in a solution of hexadecylthiosulfate (THF, 0.1 M Bu₄NBF₄). The increase in mass is substantially larger, by about an order of magnitude, than one would expect for a single monolayer of hexadecanethiolate. Further, as demonstrated in Figure 12, the mass continued to increase monotonically during repetitive scans as more charge was passed. We note that the data in Figure 12 were collected after the anodic peak in successive voltametric scans had decreased to a nearly constant level (see Figure 3). These results are consistent with electrolysis resulting in the deposition of an insoluble product.

Under conditions where a deposition process obeys the Sauerbrey relationship³¹ by forming a thin, homogeneous, and rigid film and the number of electrons transferred in the redox reaction is known, it is possible to calculate the molecular weight of the species being deposited from the

(31) For measurement of interfacial processes at electrode surfaces with an electrochemical quartz crystal microbalance, see: Buttry, D. A.; Ward, M. D. *Chem. Rev.* **1992**, *92*, 1355.

slope of Figure 12. In our case, under the conditions described in Figure 12 and assuming a one-electron oxidation (see Scheme 1), we determine a molecular weight of 89 ± 6 g/mol, less than expected for Na_2SO_4 (142 g/mol) or for NaHSO_4 (119 g/mol). This discrepancy is likely due to the poor coupling between the resonating quartz crystal and the deposited sulfate thereby reducing sensitivity.³¹ These results were not unexpected because adhesion of crystals deposited on the surface of a methyl-terminated SAM should be poor. Indeed, when extensive electrolysis was carried out at an electrode either positioned so that gravitation could cause deposits to fall from the surface or immersed in a stirred solution, the insoluble product of the reaction was found suspended in solution.

One advantage of this electrochemical synthesis of SAMs is that clean gold is not required to form complete monolayers. To demonstrate this feature in a dramatic way, two *dirty* gold electrodes were prepared by soaking in pump oil, followed by rinsing using hexanes and THF and drying with a stream of N_2 . A good monolayer ($\theta_a = 44^\circ$ for hexadecane) was obtained on one of these electrodes after 100 pulses to 1.10 V with tetradecylthiosulfate. However, even 24 h of immersion in a 50 mM solution of hexadecanethiol in ethanol gave only an incomplete monolayer, with a 37° contact angle of hexadecane. These data suggest that either the potential pulses removed contamination from the gold electrode or the applied potential served to "drive" the alkylthiosulfate ion through the contamination and thereby displace it.

Partial Formation of SAMs by Reduction in Aqueous Solution. Cyclic voltammetry in a 10 mM aqueous solution of dodecylthiosulfate in phosphate buffer (0.1 M, pH 7) at a gold electrode produced no oxidation attributable to the Bunte salt (-0.20 to 1.20 V for 4 cycles, -0.20 to 1.40 V for 4 cycles, and then -0.20 to 1.80 V for 4 cycles). The gold electrode remained wettable by hexadecane after cyclic voltammetry.³² Bunte salts are, however, known to be reducible to the corresponding thiol, so we then tried cyclic voltammetry in the opposite direction, to more negative potential. Four cyclic scans from 0.00 to -1.10 V were applied, after which the resulting gold electrode had a contact angle of hexadecane of 40° , indicating adsorption of a mostly complete monolayer. For comparison, hexadecane completely wet a separate gold surface immersed overnight in a 10 mM solution of dodecylthiosulfate in water. Spontaneous chemisorption of Bunte salts in aqueous solution to form SAMs reportedly does not occur unless the solutions are deaerated.²⁸

We also followed the growth of SAMs from a shorter-chain Bunte salt, octylthiosulfate, by measuring the wettability by hexadecane as a function of the number of cathodic pulses to -1.10 V. In these experiments, the potential was stepped from 0.00 to -1.10 V for various periods and stepped back to resting potential for a different amount of time. Table 2 summarizes the experimental parameters and the contact angles of hexadecane on the resulting monolayers. Twenty 5-s pulses to -1.10 V gave a SAM with a contact angle of hexadecane of only 30° . One hundred 1-s pulses to the same potential also gave a SAM with a hexadecane contact angle of only 30° . Contact angles of hexadecane increased slightly to 33° when the number of pulses to -1.10 V was increased to 600. Anodic pulses to 1.0 V did not change the wettability

Table 2. Contact Angles of Hexadecane (HD) on SAMs Formed by Electrolysis of Octylthiosulfates under Different Experimental Conditions

	no. of pulses	resting potential	applied potential (V)	pulsing time (s)	interval (s)	θ_a (HD)
reduction 1	20	0	-1.10	5	5	30^a
reduction 2	100	0	-1.10	1	5	30
reduction 3	600	0	-1.10	1	1	33
oxidation 1	10	0	1.00	5	6	<10

^a A strong unpleasant odor, presumably octanethiol, emanated from the cell after the potentiometric pulsing was done.

of the gold electrode. For comparison, a complete monolayer would be expected to have a contact angle of hexadecane of $\sim 40^\circ$.²⁶ One possible complication in preparing SAMs by reduction could be competing processes, such as reductive desorption of previously adsorbed thiolate species.

Conclusions

Self-assembled monolayers were prepared by electrolysis of alkylthiosulfates in THF in the presence of tetrabutylammonium tetrafluoroborate as the supporting electrolyte. The tetrafluoroborate ion was found to inhibit the spontaneous chemisorption of alkylthiosulfate onto gold, and thus SAMs only formed when a sufficiently anodic potential was applied. Cyclic voltammetry produced ordered monolayers, as long as the limiting upper voltage was not greater than ~ 1.30 V. Likewise, potentiometric pulses could also be used to produce complete monolayers selectively in the presence of the tetrafluoroborate ion. The degree of completeness of the resulting monolayers depended on the potential and the number of pulses applied. A partial monolayer was formed when pulses to low potential were applied, and we attribute this result to an insufficient driving force for ion migration and/or electron tunneling through a partial film. At optimum potentials, however, a monolayer can be formed quickly, using only twenty 5-s pulses.²⁰ Use of a higher potential (1.60 V), however, gave monolayers with low coverage due to oxidation of the gold, the SAM, or the solvent. The dependence of the optimum potential upon alkyl chain length is consistent with the ion-migration and/or electron-tunneling hypothesis.

Coupled electrochemical-QCM measurements demonstrated the deposition of an insoluble side-product of the electrolysis. Spectroscopic evidence using both XPS and Fourier transform infrared spectroscopy indicated that this insoluble material was a sulfate salt. Specifically, sulfur 2p photoemission in the XPS spectrum of a SAM that had been rinsed with only THF indicated the presence of both thiolate (monolayer) and sulfate (side-product) sulfur. An infrared spectrum of the product in a bulk electrolysis confirmed this assignment. These results are consistent with the mechanism in Scheme 1. Finally, preliminary results indicate that at least partial monolayers can be formed by electrolysis in aqueous solutions, though by reduction rather than by oxidation.

Acknowledgment. We gratefully acknowledge partial funding from the Polymer Interfaces Center, an Industry/University Cooperative Research Center at Lehigh sponsored by the National Science Foundation, and from Lehigh University. We also thank A. Miller for assistance with the XPS and A. Gilicinski (Air Products Corp.) for use of the QCM.

(32) A recent paper reported the formation of partial layers on gold by oxidation of a hydroquinone-containing Bunte salt from aqueous solution (ref 21).