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Direct Route to Well-Defined, Chemically Diverse Electrode Arrays

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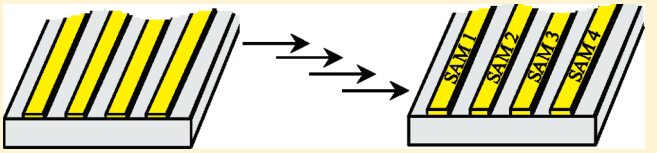
ABSTRACT: The selective placement of molecules of interest at specific locations on surfaces is a keystone for the bridge between interfacial science and technology. One approach to this problem is the use of electrochemistry to direct interfacial reactions that immobilize species from solution onto surfaces. In this study, sets of individually functionalized gold electrodes were formed by the selective formation of monolayers from four different alkyl thiosulfates. Analysis of the arrays using spatially resolved X-ray photoelectron spectroscopy (XPS) revealed each type of functionality exclusively on the electrode to which it was directed. The wetting behavior of these surfaces was also consistent with homogeneous monolayers placed selectively on each electrode. The flexibility of this method provides the ability to produce a wide variety of chemical patterns at interfaces of interest for a range of technological applications.



INTRODUCTION

A range of emerging technologies—eNoses, eTongues, biosensors, etc.—rely on an ability to prepare an array of electrodes that are chemically differentiated from one another and well-defined with respect to structure and composition.[1−11] Spontaneous self-assembly of alkanethiols or dialkyl disulfides on gold provides a facile method for uniform coverage of the metal surface with a well-defined monolayer of the organosulfur species,[12−17] but does not generally provide a direct route for selectively modifying substrates containing two or more gold features (e.g., a microelectronic chip).[18] This problem limits the usefulness of self-assembly for differentiating interfacial structure, for example, in electrode arrays for sensor applications.

To address this problem, we developed an alternative approach for the activated adsorption of self-assembled monolayers (SAMs) on gold—electrochemical oxidation of alkyl thiosulfates at a gold electrode—which allows the directed formation of an alkyl thiolate monolayer selectively on one electrode in the presence of others.[19,20] The apparent stoichiometry of this reaction is provided in eq 1.[19−21] This method has recently been

$$RSSO_3^- + Au \xrightarrow{-e^-} RS\text{-}Au + SO_3 \qquad (1)$$

extended to include a broad range of terminal functionality,[21] as well as mixed monolayers.[22] In this paper, we report the successful direct modification of *multiple* electrodes or microelectrodes, each with a different SAM, on a single substrate. Spatially resolved X-ray photoelectron spectroscopy (XPS)—a technique sensitive to small amounts of cross-contamination—was used to verify the compositional integrity of each SAM.

Other methods have been used to control the adsorption of thiolate SAMs in systems having various levels of complexity. For example, a thiolate SAM can be allowed to form on one electrode, while preventing unwanted adsorption on an adjacent electrode by applying a cathodic potential.[23,24] Hydrazides or diazonium salts have also been used for the selective modification of electrodes.[25,26] In addition, indirect methods for producing different SAMs on neighboring gold electrodes have been reported. For example, if a SAM is adsorbed on a set of electrodes, and then removed from one of the electrodes by reductive or oxidative desorption, a second SAM can be added to the vacated surface.[27−40] The presence of particular species on functionalized electrodes in these systems has been inferred using a variety of techniques,[24,29−38] and in a few cases verified by spectroscopic methods sensitive to elemental composition or characteristic fragmentation.[23,27,28,39,40]

The goal of producing a set of electrodes that is both chemically diverse and well-defined requires that neighboring electrodes be modified sequentially without the SAMs added later in the sequence disrupting or removing those added earlier. An advantage of electrochemisorption of monolayers from alkyl thiosulfates is that it allows rapid, direct, and regioselective placement of ω-functionalized SAMs without the complication of cross-contamination due to either adsorption at neighboring electrodes or thiol-exchange reactions with SAMs that had been previously adsorbed.[41] Hence, electrically isolated electrodes—a separate gold-coated slide or neighboring microelectrodes on a chip—do not adsorb monolayers during the electrosynthesis of a SAM elsewhere in the same solution.[20] The short time required for formation of a monolayer in this way (~7 min) is helpful in reducing the risk of cross-contamination. Furthermore, this method does not rely on the use of SAMs that contain groups (e.g., oligoethylene glycol) that resist contaminating adsorption.

EXPERIMENTAL SECTION

General. Tetra-*n*-butylammonium tetrafluoroborate (TCI, 98%), ethanol (Anhydrous, JT Baker, 95%), silver nitrate (Fisher, 99.8%), and sodium thiosulfate pentahydrate (Alfa Aesar, 99%) were used as received. Acetonitrile (Acros, 99.8%) and tetrahydrofuran (THF,

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Mallinckrodt, 99%) were purified and dried using a Pure Solv system (Innovative Technology, Inc.). Water was purified with a Purelab Prima system (Elga) to a resistivity of ~0.3 MΩ cm. Hydrogen peroxide (30%) and sulfuric acid (≥95%) were used as received from EMD. Hexadecane (99%, Aldrich) was passed through activated alumina twice before use in contact-angle measurements. Syntheses for the alkyl thiosulfates used in this work have been reported separately.[21]

Macroscopic Four-Electrode Sample. A glass microscope slide was cleaned with piranha solution and then partially masked by three parallel strips of polyimide tape. *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.* The width of both the exposed lines and the spaces between them was ~3.2 mm. Approximately 50 Å of Ti (as an adhesion promoter) and then 2000 Å of Au were evaporated onto the glass slides. The tape was removed prior to elecrochemical experiments.

Microelectrode Array. Prior to SAM formation, a triple-track tester (TTT) was cleaned with UV−ozone for 30 min, soaked in ethanol for 30 min to reduce the resulting gold oxide, rinsed with deionized water (3 MΩ cm), and dried under a stream of nitrogen.[42] Ozone was generated at atmospheric pressure in an ozone cleaner (UVOCS Inc.) with a dual wavelength source (λ = 254 and 185 nm). The triple-track tester was a generous gift from AT&T Bell Laboratories (previous company name).[20]

Formation of SAMs on Electrode Arrays. To form a SAM, 40 potentiometric pulses from −0.9 to 1.1 V, with 5 s at each potential, were applied to a gold electrode. The electrochemical cell used in these experiments comprised a gold working electrode, a platinum counter electrode, and a silver/silver nitrate reference electrode immersed in a THF solution of the alkyl thiosulfate (1 mM) and tetra-*n*-butylammonium tetrafluoroborate (0.1 M). The reference electrode consisted of a silver wire inside a glass tube fitted with a Vycor frit and filled with a 3 mM solution of silver nitrate in acetonitrile. After each step-potential sequence, the electrode array was rinsed with THF, ethanol, and water and then dried under a stream of nitrogen.

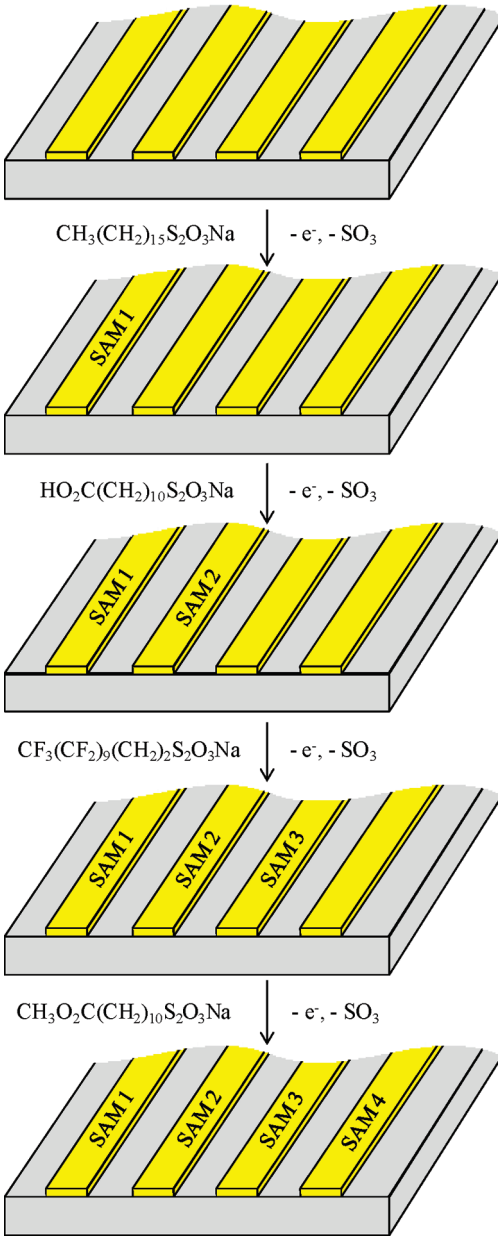
Fluorescence Microscopy. An Olympus CX41 microscope equipped with a CX-DMG-2 filter module was used to observe the dewetting of Rhodamine 6G using the 4× objective. Images were taken with an Edmund Optics EO- 1312 M CMOS monochrome USB camera fitted to the microscope. Color was added across the entire image using *Igor Pro* (version 6.03) to approximate what was observed through the eyepiece.

X-ray Photoelectron Spectroscopy. Spectra were collected with a Scienta-300 spectrometer. Monochromatic Al Kα X-rays were generated using a rotating anode and photoemission monitored with a 300-mm-diameter hemispherical analyzer. To analyze the four-electrode array, high-resolution spectra were collected in the C 1s and Au $4f_{7/2}$ regions using normal mode at a 20° takeoff angle between the sample surface and the path to the detector. For this sample, 3−5 scans were collected at a pass energy of 300 eV in the carbon region, and two scans were collected at a pass energy of 75 eV in the gold region. To analyze the microelectrode array, a map of the F 1s photoemission across the sample was collected in high-spatial-resolution-lens mode at a 90° takeoff angle. For this sample, 300 sweeps with a pass energy of 300 eV were acquired. CasaXPS software was used to analyze the photoemission spectra.

RESULTS AND DISCUSSION

A set of four electrodes were prepared on a single substrate by evaporating gold onto a glass microscope slide partially masked by three parallel strips of polyimide tape. The width of both the gold lines and the spaces between them was ~3.2 mm. Monolayers were formed sequentially on each working electrode by applying 40 potentiometric pulses in solutions containing one of the following ω-functionalized alkyl thiosulfates, $X(CH_2)_nSSO_3Na$: X = CH_3, n = 15; X = n-$C_{10}F_{21}$, n = 2; X = CO_2H, n = 10; and X = CO_2CH_3, n = 10.[20] This process is shown schematically in Scheme 1. Each potentiometric pulse involved stepping the potential from −0.9 to 1.1 V, with 5 s at each potential. After each SAM was added, the electrode array was rinsed with THF, ethanol, and water, and then dried under a stream of nitrogen. The electrosynthesis was then repeated on an adjacent electrode in a freshly prepared solution containing a different alkyl thiosulfate. This process was repeated until all four electrodes had been modified. The order of placement of the SAMs, from one side of the substrate to the other was as follows: electrode 1, alkyl; electrode 2, carboxylic acid; electrode 3, perfluoroalkyl; and electrode 4, methyl ester.

Scheme 1. Schematic Illustration of the Sequential Modification of Four Gold Electrodes, Each with a Different Monolayer, on a Single Glass Substrate[a]



[a] For clarity, the electrodes and glass slides are not drawn to scale.

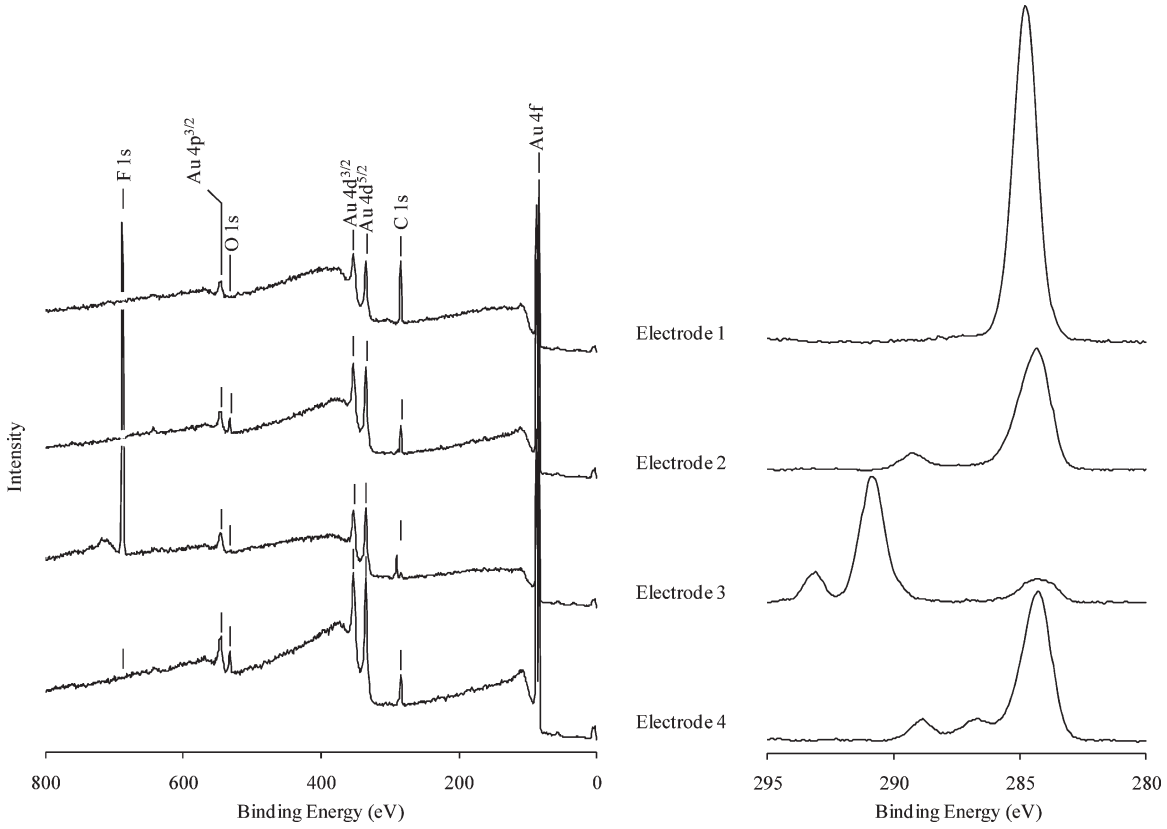


Figure 1. Survey (left) and high-resolution C 1s (right) X-ray photoelectron spectra of electrochemically directed SAMs derived from RS_2O_3Na precursors on gold electrodes: Electrode 1, R = $CH_3(CH_2)_{15}$; Electrode 2, R = $HO_2C(CH_2)_{10}$; Electrode 3, R = $CF_3(CF_2)_9(CH_2)_2$; and Electrode 4, R = $CH_3O_2C(CH_2)_{10}$.

The choice of adsorbate precursors containing varied functionality allowed straightforward analysis by XPS, which could be used to verify the presence or absence of heteroatoms in these functional groups. In addition, the carbon 1s photoemission from SAMs prepared from these precursors are easily distinguishable, due to differences in binding energy of saturated alkyl carbons, perfluorinated carbons, the carboxyl carbon of the acid, and the ether carbon of the ester. The specific questions addressed by XPS in this study were: did the SAM on a particular electrode correspond to the alkyl thiosulfate from which it was derived, and was there any evidence of cross-contamination of the SAM by components adsorbed at neighboring electrodes?

Survey spectra (Figure 1, left) confirmed the presence of oxygen only on electrodes 2 and 4, where SAMs terminated by carboxylic acid and methyl ester groups had been placed, respectively. Likewise, fluorine was only observed in the survey spectrum of electrode 3. High-resolution spectra in the C 1s region of each electrode revealed peaks with binding energies consistent with the functionality expected on that electrode (Figure 1, right).[21] Electrode 1 contained no oxidized carbon species, as expected. The spectra of electrodes 2 and 4 contained peaks at high binding energy, consistent with the presence of carboxylic acid (289.2 eV, carboxyl) and methyl ester (286.6 eV, methyl; 288.9 eV, carboxyl), respectively.[21] And finally, the spectrum of electrode 3 contained three peaks at high binding energy, consistent with a partially fluorinated alkyl chain (293.2 eV, CF_3; 290.9 eV, CF_2; 284.3 eV, CH_2).[21]

Contact angles of water and of hexadecane measured on each electrode after it was functionalized were also consistent with selective placement of individual SAMs, with little or no contamination of neighboring electrodes (Table 1). Thus, when a SAM was formed on a particular electrode, the neighboring unmodified electrode remained wettable by hexadecane—consistent with adsorption on the former but not the latter. Likewise, formation of a SAM on a particular electrode had little or no effect on the wettability of a different SAM that had previously been formed on an adjacent electrode.

Having demonstrated the regioselectivity of this method on easily characterized macroscopic electrodes, we extended our work to include a more technologically relevant microelectrode array. The chip comprised a serpentine pattern of three gold microelectrodes (50 μm wide) separated by 100 μm spacings on an alumina substrate. A different SAM was formed on each microelectrode, using three of the same alkyl thiosulfates described above, in the following pattern: electrode A, alkyl; electrode B, carboxylic acid; and electrode C, perfluoroalkyl. We analyzed the array in two steps. First, the carboxylic-acid-terminated SAM could be differentiated from the other two hydrophobic SAMs by selective dewetting of the latter by a thin film of an aqueous solution of a fluorescent dye (Rhodamine 6G).[20] A fluorescence micrograph revealed dark lines where the dye solution had dewet the electrodes bearing alkyl and perfluoroalkyl SAMs and lighter lines where a fluorescent wetting film covered the electrode bearing a carboxylic-acid-terminated SAM (Figure 2, top). The two hydrophobic electrodes could be differentiated from one another by spatially resolved X-ray photoelectron spectroscopy. A map of F 1s photoemission across the electrode array was obtained using the high-spatial-

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Table 1. Contact Angles on Sequentially Modified Electrodes Functionalized from Alkyl Thiosulfate Precursors, RS_2O_3Na[a]

step	R	θ_a HD[b] electrode 1	θ_a H_2O electrode 2	θ_a HD electrode 3	θ_a H_2O electrode 4
1	$(CH_2)_{15}CH_3$	**46**			
2	$(CH_2)_{10}CO_2H$	46	**54**		
3	$(CH_2)_2(CF_2)_9CF_3$		53	**78**	
4	$(CH_2)_{10}CO_2CH_3$			78	**74**

[a] Values in bold refer to the electrode modified in that step; those in normal text refer to a re-measurement on the electrode modified in the preceding step. [b] Contact angles of hexadecane. All contact angles are in degrees.

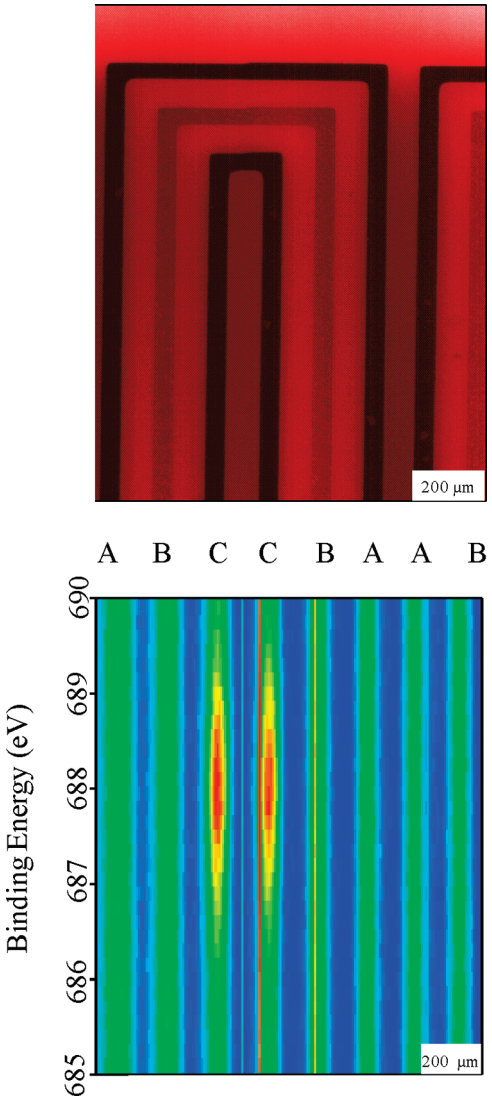

Figure 2. (Top) Fluorescence micrograph of a chemically modified triple-track tester, covered with a thin film of ~1 mM Rhodamine 6G (aq). Electrode B was electrochemically modified with a hydrophilic monolayer (carboxylic acid) and remains coated by the thin aqueous film. Electrodes A and C were electrochemically modified with hydrophobic monolayers (alkyl and perfluoroalkyl, respectively) and were dewet by the dye solution. (Bottom) An image generated from spatially resolved high-resolution XPS data collected in the F 1s region. Only the horizontal axis defines spatial position across the chip; the vertical axis defines binding energy of the photoemission. The intensity scale from low to high on the gold electrodes corresponds to the color gradient from green to red, respectively.

resolution-lens mode. This measurement revealed the presence of fluorine only on the electrode expected to bear the fluorinated SAM (Figure 2, bottom), with little or no fluorine on the neighboring electrodes. The variation in inelastic background intensity in the map results from the large difference in photoemission cross section between gold and alumina and allows visualization of the gold lines (green) and alumina spaces (blue). Variations in the widths of these lines and spaces are due to a combination of the spatial resolution of the spectrophotometer (~25 μm) and an incident X-ray spot maximum that is not coincident with the electron-optic axis of the lens. The vertical axis in this figure represents binding energy of the photoemission, not distance along a vertical direction.

The approach described in this paper provides a rapid and direct route to chemically diverse electrode arrays relevant to the development of a range of sensor and device technology. This method for preparing SAMs on selected gold features provides exquisite control of the chemical complexity of the patterns that can be produced. For example, in addition to the variety of single-component SAMs that can be adsorbed, mixed monolayers are also accessible and have compositions that mirror the solutions from which they were formed.[22] Furthermore, varying the number of potentiometric pulses can be used to control the completeness of the SAMs adsorbed.[19] Coupled with the spatial selectivity demonstrated in this paper, these degrees of freedom provide access, at least in principle, to an arbitrarily large number of patterned surfaces.

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