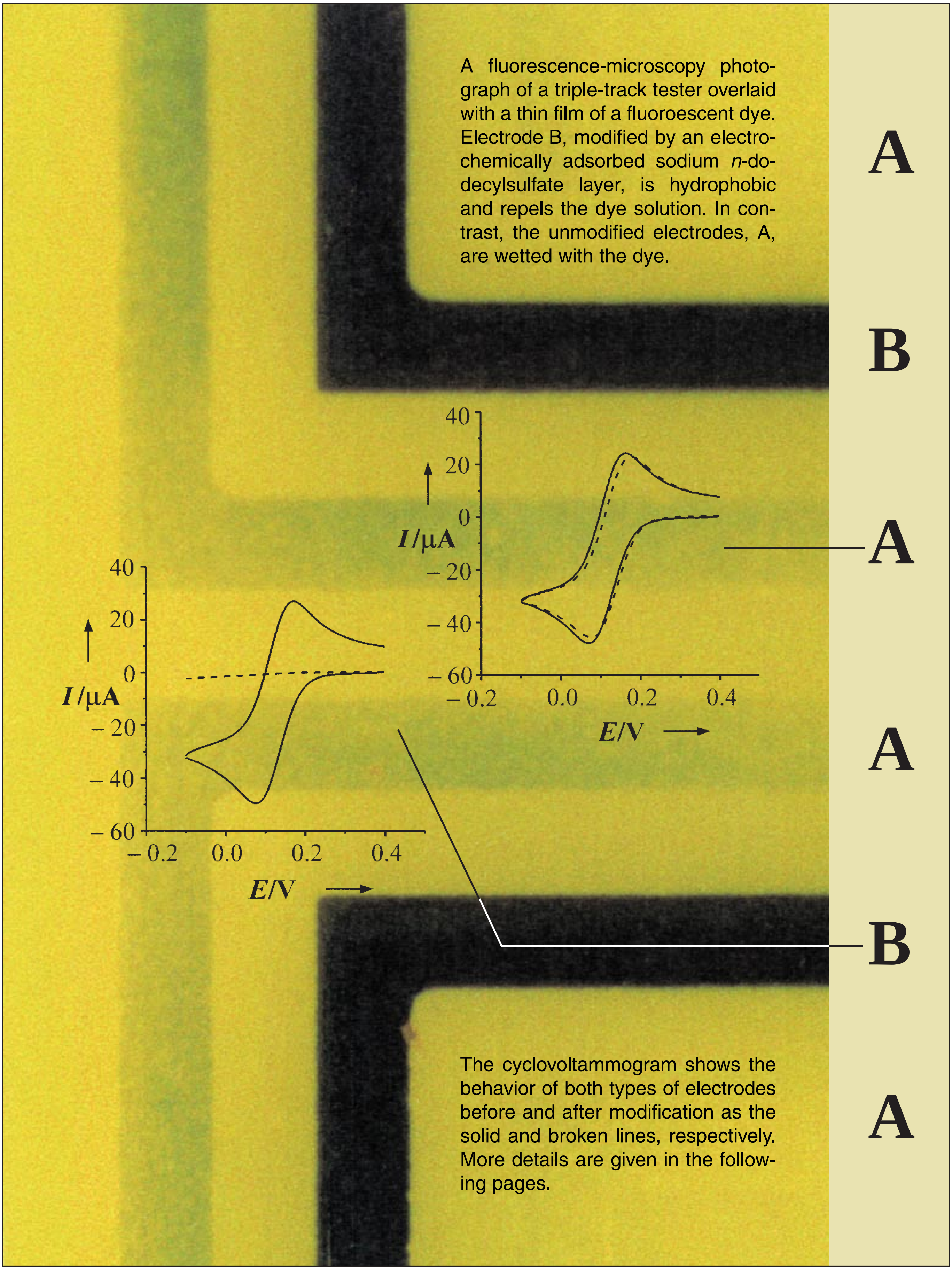

A fluorescence-microscopy photograph of a triple-track tester overlaid with a thin film of a fluoroescent dye. Electrode B, modified by an electrochemically adsorbed sodium *n*-dodecylsulfate layer, is hydrophobic and repels the dye solution. In contrast, the unmodified electrodes, A, are wetted with the dye.

The cyclovoltammogram shows the behavior of both types of electrodes before and after modification as the solid and broken lines, respectively. More details are given in the following pages.

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Electrochemically Directed Self-Assembly on Gold**

Chen-Chan Hsueh, Mong-Tung Lee,
Michael S. Freund,* and Gregory S. Ferguson*

One of the most attractive characteristics of self-assembled monolayers (SAMs) is the simplicity of their preparation: simply expose a substrate surface to an appropriate adsorbate.[1–3] This facility unfortunately prevents selective monolayer formation on particular substrates in the presence of others of the same composition. While contact printing of SAMs has proven useful in preparing mesoscale patterns on various substrates,[4] the formation of monolayers on particular features of a preexisting pattern—such as an electrode array, an integrated circuit, or a microelectronical systems (MEMS) device—remains challenging. Advances have been made using the oxidation of alkyl thiolates on gold electrodes to control the formation of SAMs,[5] and reductive desorption[6, 7] of monolayers from modified electrodes.[8] In this paper, we report a new method for forming SAMs by the electrochemical oxidation of alkyl thiosulfates on gold electrodes and demonstrate their selective formation in specific locations on a set of closely spaced microelectrodes.[9]

The chemical[10–13] or electrochemical[14, 15] oxidations of alkyl thiosulfates (Bunte salts) are known to produce disulfides. We hypothesized that the proposed intermediate of the electrochemical reaction, an alkylsulfide radical,[14] or the disulfide produced at a gold electrode could be trapped and form stable gold–thiolate bonds.[16] In preliminary experiments,[17] this synthetic strategy resulted in the successful formation of a SAM on a gold electrode in a Galvanic cell, in which iodine was used as a remote oxidant in an aqueous solution. A monolayer did not form under analogous open-circuit conditions. Using a Galvanic cell or potentiometic conditions to drive the oxidation of alkyl thiosulfates in an aqueous solution did not provide adequate reproducibility or control over the electrochemisorption process. These results prompted us to explore the use of nonaqueous systems to characterize the redox chemistry involved.

Figure 1a shows a cyclic voltammogram of sodium *n*-hexadecylthiosulfate in THF at a gold electrode. The inset magnifies the range from -0.80 to $+0.50$ V (versus Ag/$AgNO_3$) of the anodic scan. Clearly, the onset of current flow begins at about -0.50 V. For the results shown in Figure 1b, a gold electrode was immersed into the sodium *n*-hexadecylthiosulfate solution and its potential stepped from -0.90 V to a particular value in the range producing an anodic current. After 5 s at this potential, it was stepped back to the -0.90 V resting potential. This process was repeated using a separate sample for each potential. The advancing contact angle of hexadecane provided a convenient measure of the degree of completeness of the resulting monolayer films as a function of the applied potential and number of pulses used in their formation. In all cases, the onset of anodic current at about -0.50 V corresponded closely with the appearance of a finite contact angle of hexadecane on the film produced. The peak contact angles (45–47°) compared favorably with those reported for complete, well-ordered SAMs prepared by the self-assembly of hexadecanethiol.[2] The loss of lipophobicity at higher potentials corresponded to a strong anodic current (Figure 1a), probably reflecting oxidation of the thiolate groups, the gold electrode, or THF, and concomitant disordering of the films.

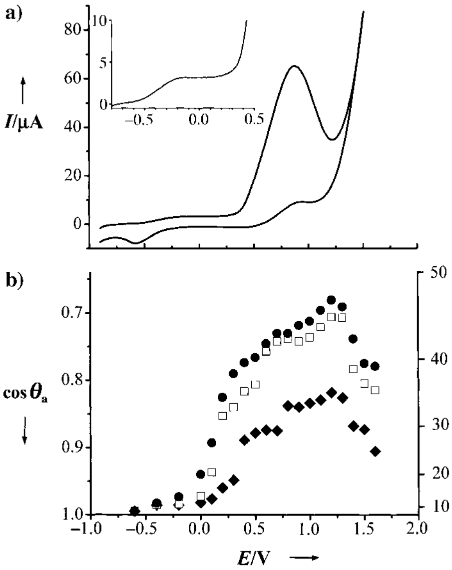

Figure 1. a) Cyclic voltammogram for a 10 mM solution of sodium hexadecylthiosulfate in THF (0.1M Bu_4NBF_4, 100 mVs^{-1}) using a gold working electrode and a Ag/$AgNO_3$ reference electrode (3 mM in CH_3CN). Inset: the onset of current flow in the anodic scan. b) Advancing contact angles of hexadecane on SAMs formed by electrochemical oxidation of hexadecylthiosulfate using one (◆), three (□), and five (●) voltametric pulses to different potentials.

We followed the growth of monolayers formed at 1.20 V as a function of the number of potentiometric pulses by monitoring monolayer thickness and wettability. As the number of pulses was increased on a single electrode, the contact angles of both water and hexadecane rose (Figure 2b)

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[*] Prof. M. S. Freund,[+] Prof. G. S. Ferguson,[++] Dr. C.-C. Hsueh, M.-T. Lee
Department of Chemistry
Lehigh University
6E. Packer Avenue, Bethlehem, PA 18015 (USA)
Fax: (+1)610-758-6536
E-mail: msf@its.caltech.edu, gf03@lehigh.edu

[+] Current address:
Beckman Institute, Mail Code 139-74
California Institute of Technology
1200E. California Boulevard, Pasadena, CA 91125 (USA)
Fax: (+1) 626-564-9672

[++] Further address:
Department of Materials Science & Engineering
Lehigh University
5E. Packer Avenue, Bethlehem, PA 18015 (USA)

[**] We gratefully acknowledge partial funding from the Polymer Interfaces Center, an Industry/University Cooperative Research Center at Lehigh University, sponsored by the National Science Foundation and Lehigh University. We thank AT&T Bell Laboratories (now Lucent, Inc.) for a gift of the triple-track testers. We also thank A. C. Miller for assistance with the XPS measurements, L. Lowe-Krentz for allowing the use of the fluorescence microscope and G. Freund for translating the manuscript into German.

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

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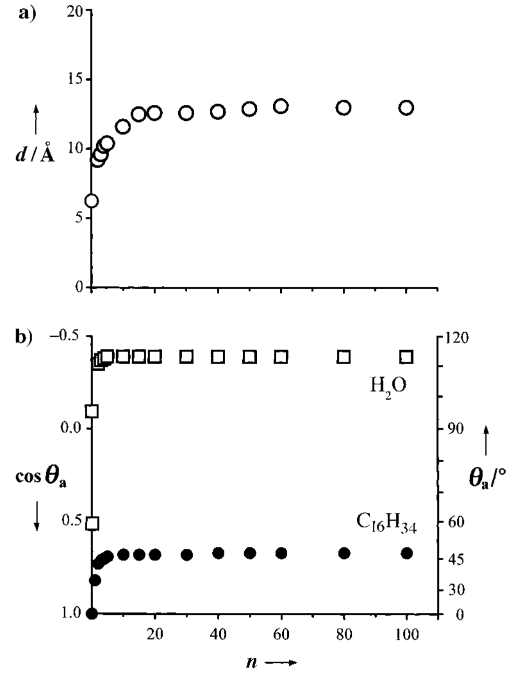

Figure 2. a) Ellipsometric thickness d and b) advancing contact angles θ_a of water and of hexadecane on a gold electrode as a function of the number n of potential pulses (1.20 V versus $Ag/AgNO_3$) in a 10 mM solution of sodium n-hexadecylthiosulfate in THF (0.1M Bu_4NBF_4).

and reached limiting values consistent with a well-ordered monolayer (water 112–114°; hexadecane 45–47°).[2] The ellipsometric thickness of the monolayer also increased as a function of the number of pulses to approximately 13 Å (Figure 2a). A monolayer formed at the same time by self-assembly of hexadecanethiol had the same thickness. X-ray photoelectron spectra of a monolayer formed by the electrolysis of hexadecylthiosulfate at 1.20 V (five pulses) and of one formed by adsorption of hexadecanethiol from ethanol were nearly indistinguishable.[18] High-resolution spectra (sulfur 2p region) showed that both samples contained only thiolate sulfur; no evidence indicated higher oxidation states arising from either incomplete reduction of the thiosulfate or oxidation of the thiolate by air.[18, 19]

The key advantage of this electrochemical synthesis over the conventional chemisorption of alkanethiols and -disulfides is that it provides *selectivity* in the placement of a SAM only on electrodes with potentials high enough to oxidize the thiosulfate precursor. We demonstrated this feature by selectively modifying one electrode in the close proximity of another: The samples used in these studies were triple-track testers,[20] comprising a serpentine pattern of three 70–80-μm wide gold lines spaced 70–80 μm apart on an alumina substrate. The two outer lines (electrode A) were connected at one end; the central line (electrode B) was electronically isolated. The device was immersed into a 10-mM sodium n-dodecylthiosulfate solution (THF, 0.1M Bu_4NBF_4) and the potential of electrode B was stepped from −0.90 V (versus $Ag/AgNO_3$) to +0.90 V. After 200 ms at this potential, it was stepped back to the −0.90 V resting potential. This process was repeated through 150 pulses, with a interval of 6 s between pulses; electrode A was electronically isolated throughout this process. The differences between this protocol and that used to form the SAMs of hexadecylthiosulfate (Figures 1 and 2) reflect optimization to minimize cross-contamination of the nearby electrode in this experiment, as well as the difference in the chain lengths (C_{12} versus C_{16}) of the precursors.

This process left the two electrodes on the device strongly differentiated, both in surface energy and electrochemical activity. Figure 3 shows a fluorescence micrograph (×100 magnification) of the device coated with a thin layer of a 1.06 mM aqueous solution of the fluorescent dye rhodamine-6G. The modified electrode B repels the solution and thus appears black due to the absence of the dye. The unmodified electrode A is coated with the dye solution and thus appears greenish-yellow. Below the micrograph in Figure 3 are cyclic voltammograms for a second triple-track tester immersed in aqueous solutions of ferricyanide, before and after electrode modification. The modified electrode B showed a normal response prior to modification but was electrochemically inactive after coating with a dodecanethiolate monolayer. In contrast, the response of the unmodified electrode A at this scan rate did not change significantly before and after treatment of electrode B.

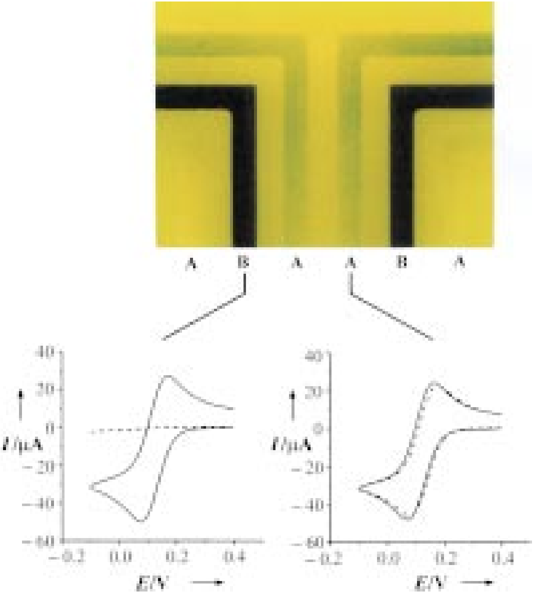

Figure 3. Top: A fluorescence micrograph (×100 magnification; Nikon Microflex UFX-II microscope; Nikon FX35a camera) of a triple-track tester covered with a thin layer of a 1.06 mM aqueous solution of the fluorescent dye rhodamine-6G. The central electrode (B) is hydrophobic resulting from electrochemisorption of sodium n-dodecylthiosulfate and repels the dye solution. The outer electrode (A; two outer lines) is unmodified and covered by the dye solution. Both the widths of the gold lines and the spacings between them were in the range of 70–80 μm. Under: cyclic voltammograms (1.0 mM $K_3Fe(CN)_6$, 0.1M KCl, scan rate 100 mV s^{-1}; silver quasi-reference electrode, AgQRE) beneath the micrograph show the responses of both electrodes before (——) and after (----) modification of the electrode B.

In contrast to these electrochemically directed adsorption processes, treatment of a gold electrode by solutions of hexadecylthiosulfate in THF with (90 h) or without (5 min) Bu_4NBF_4 led to the spontaneous, nonselective adsorption of a

SAM.[9] This kinetic inhibition towards spontaneous adsorption was not observed when Bu_4NPF_6 was used instead of Bu_4NBF_4. The rate of spontaneous adsorption in the presence of tetrafluoroborate is sufficiently slow to allow the selective electrochemisorption described herein.

We have developed an electrochemical method for the selective formation of self-assembled monolayers on a particular gold electrode in the presence of another nearby electrode. The monolayers produced are very similar in thickness, wettability, blocking of heterogeneous electron transfer, and elemental composition to analogous SAMs formed by the chemisorption of alkanethiols. The selectivity of this synthetic method should allow the preparation of microelectrode arrays with differentiated surface chemistry, a goal of great importance in the fabrication of sophisticated sensor arrays.[5–7, 21, 22] Other attractive features of this electrosynthesis of SAMs are: a) the control it provides over the degree of coverage; b) the short time (less than a minute) needed to form a SAM; c) the ability to form SAMs easily on gold that is not freshly evaporated; and d) the use of precursors without an unpleasant odor (for precursor alkyl groups containing more than about ten carbon atoms). The formation of SAMs by the electrochemical oxidation of alkyl thiosulfates may be extendable to other metals, as long as anodic dissolution of the metal does not interfere at the potential necessary to oxidize the Bunte salts. In preliminary experiments, we found that SAMs can also be formed from aqueous solutions by the reduction of an alkyl thiosulfate, a process known to produce thiols.[10]

Received: September 22, 1999 [Z14044]

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Building Supramolecular Nanostructures at Surfaces by Hydrogen Bonding**

Johannes V. Barth,* Jens Weckesser, Chengzhi Cai, Peter Günter, Lukas Bürgi, Olivier Jeandupeux, and Klaus Kern*

Supramolecular structures formed by the self-assembly of functional molecular building blocks are a promising class of materials for future technologies.[1–3] Particularly useful for their fabrication is hydrogen bonding,[4] which provides both high selectivity and directionality.[5] Hydrogen-bonded archi-

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[*] Priv.-Doz. Dr. J. V. Barth, Prof. Dr. K. Kern,[+] J. Weckesser,
Dr. L. Bürgi, Dr. O. Jeandupeux
Institut de Physique Expérimentale
Ecole Polytechnique Fédérale de Lausanne
PHB-Ecublens, 1015 Lausanne (Switzerland)
Fax: (+41) 21-693-3604
E-mail: johannes.barth@epfl.ch, kern@kern.mpi-stuttgart.mpg.de

Dr. C. Cai, Prof. Dr. P. Günter
Institut für Quantenelektronik
Eidgenössische Technische Hochschule Zürich
ETH-Hönggerberg, 8093 Zürich (Switzerland)

[+] Further address:
Max-Planck-Institut für Festkörperforschung
70569 Stuttgart (Germany)

[**] Fruitful discussions with A. de Vita, B. Müller, and H. Brune are acknowleged.