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Development and Application of Thin-layer Spectroelectrochemical
Techniques for the Study of Organosulfur Monolayers Adsorbed at
Gold

by

Simmons, Neal

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Ames Laboratory, U.S. DOE

Iowa State University

Ames, Iowa 50011

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1. GENERAL INTRODUCTION

The design, construction, and characterization of chemically modified surfaces is an important topic having applications to a broad range of fields including electrochemistry, sensors and transducers, photoresists and microelectronics, biological interfaces, and corrosion inhibition^{1,2}. In particular, a large number of research efforts have focused on the modification of electrode surfaces by the attachment of thin organic films^{3,4}. These efforts have largely examined the change in specificity of the electron transfer process, the effect on the electrode/electrolyte interface, and the development of robust coating materials that impart a specific reactivity to the electrode^{3,5,6}.

One route to surface modification which has attracted a large amount of attention is the adsorption of organosulfur monolayers at gold, silver, and platinum surfaces^{2,4}. The rationale behind this modification scheme is based on work by Nuzzo and Allara, who discovered that cyclic disulfides were spontaneously adsorbed at freshly-prepared gold electrodes⁷. Characterization of these assemblies by techniques such as infrared spectroscopy, ellipsometry, and contact angle measurements indicated that stable, structurally coherent monomolecular films were formed, apparently by cleavage of the disulfide bond. These characteristics, in addition to their facile preparation, have generated interest in organosulfur-derived monolayers for more than a decade.

A main research interest of our group is the characterization of monolayers formed by the spontaneous adsorption of organosulfur compounds at gold. This dissertation describes the development and application of long optical pathlength thin-layer spectroelectrochemistry in an attempt to address key issues regarding the reactivity

of surface-immobilized molecules. The first section of this introductory chapter briefly describes the general approach to the preparation and characterization of these films. The last section provides an overview of the main principles and advantages of thin-layer spectroelectrochemistry for studying surface-adsorbed species.

Preparation and Characterization

Spontaneous chemisorption of organized monolayers occurs when a substrate is immersed in a dilute solution of a thiol, disulfide, or sulfide precursor. While the most common systems reported in the literature are formed by the adsorption of thiols at gold, other noble metals such as silver⁸⁻¹⁶, copper^{11, 17-20}, and platinum²¹⁻²³ have been studied along with disulfide^{7, 24-29} and sulfide³⁰⁻³² precursors. Gold is widely used over the other substrates because it is relatively inert to most common contaminants and does not readily form a native oxide. The evaporation of gold films onto glass or freshly-cleaved mica provides a source of fresh substrates which are relatively smooth at a microscopic level. Subsequent annealing of Au/mica substrates produces gold films with a predominant (111) surface crystallinity³³⁻³⁷.

The monolayer is divided into three functional regions as shown in Figure 1 by an idealized representation of a monolayer-liquid interface. The terminal group, by virtue of its location at the outermost portion of the film mainly affects the interfacial properties of the film, although bulky functionalities can also limit the packing of the film. Variation of the terminal functional group is often used to create a monolayer having specific interfacial properties (i.e., hydrophobic/hydrophilic, acidic/basic, etc.)³⁸⁻⁴¹. The chain/spacer region, most commonly comprised of alkyl chains, dictates to a large degree

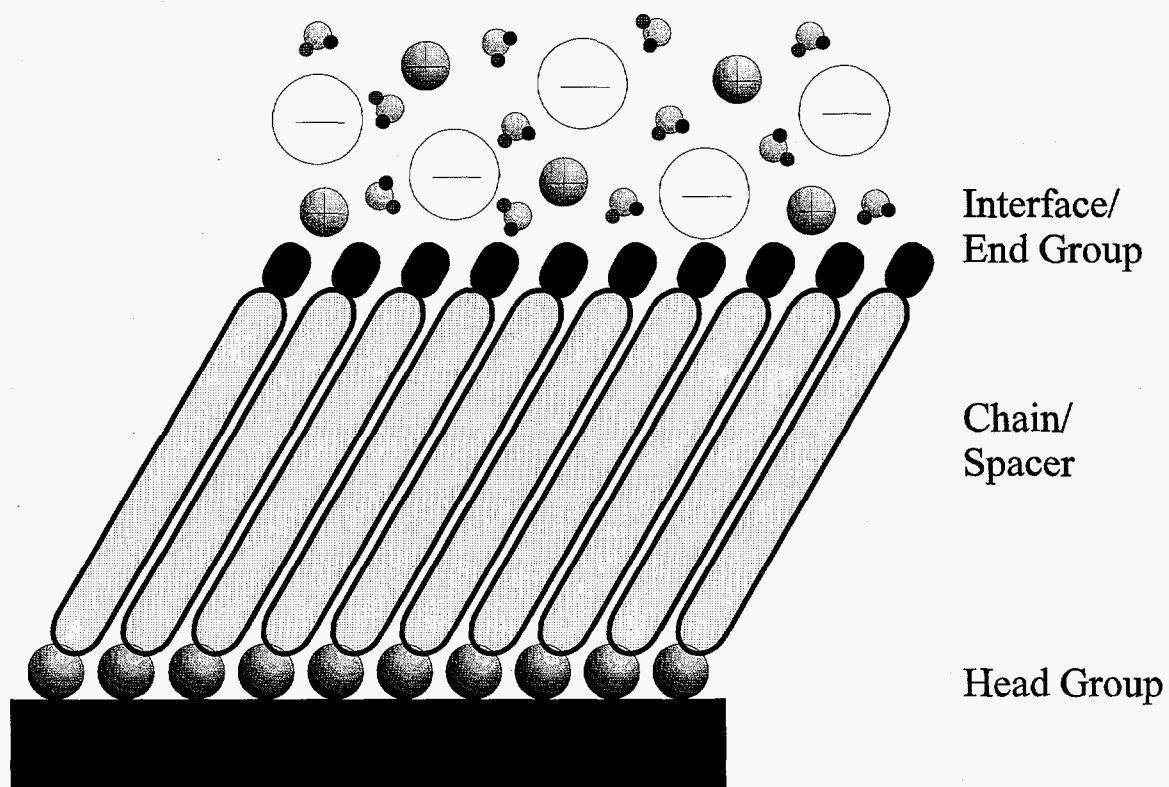


Figure 1. Idealized representation of a monolayer-solution interface.

the ordering and permeability of the monolayer. The cohesive interactions between the methylene chains are important factors in monolayer formation and directly affect the barrier properties of the film⁴¹⁻⁴³. Finally, the head group region, lying at the monolayer-substrate interface, includes all aspects of the sulfur-gold binding chemistry.

Chemisorption of organosulfur precursors at gold surfaces is driven by the formation of a gold-sulfur bond having a strength of ~ 40 kcal/mol^{4, 42, 44} which accounts to a large degree for the stabilization and robustness of these monolayers.

As organosulfur monolayers become more popular, the application of a large number of analytical techniques to study these architectures has provided a wealth of information regarding their structure and composition, which has a direct impact on their overall chemical and physical properties. Infrared reflection absorption spectroscopy (IRRAS) has been used to probe the orientation of the methylene chains and to assess their local environment (liquid- vs. solid-like)⁴⁵. The methylene chains of alkanethiols adsorbed at gold typically exist in extended, all-trans configuration sequences that are tilted at $\sim 30^\circ$ from the surface normal⁴³.

Scanning probe microscopy has indicated that alkanethiolates adsorb at a Au(111) surface forming a $(\sqrt{3} \times \sqrt{3})R30^\circ$ adlayer^{34, 46-48} which is also demonstrated by electron diffraction⁴⁹, and low temperature helium diffraction⁵⁰ experiments. Although not proven experimentally, theoretical calculations indicate that alkanethiolates adsorbed at gold reside in the three-fold hollow sites¹³.

Monolayers have been characterized by X-ray photoelectron spectroscopy (XPS) to probe the nature of the head group and the binding chemistry between the adlayer and

substrate. The location of the S(2p_{1/2}) and S(2p_{3/2}) couplet at ~161.9 and ~163.2 eV for both thiol- and disulfide-derived monolayers indicates that they are adsorbed as thiolates^{18, 25, 31, 35, 51-53}. Interestingly, films prepared from a dithiol which structurally prevents one thiol group from interacting with the gold surface exhibits two S(2p) couplets--one from the surface-adsorbed thiol and another at binding energies ~1-2 eV higher corresponding to an unbound thiol⁵⁴.

Organosulfur monolayers adsorbed at gold have been studied extensively using electrochemical techniques⁴². One area of particular interest is the study of electron transfer processes occurring across an interface. Alkanethiols incorporating electroactive functional groups such as ferrocene⁵⁵⁻⁶² and viologen⁶³ have been immobilized at electrode surfaces. These well-defined systems are ideal models for examining the effects of varying the interfacial structure on the electron transfer process.

One study focused on the electrochemical behavior of ferrocene-terminated alkanethiolate monolayers⁵⁵. The pendant ferrocene moieties behave as nearly ideal, non-interacting electroactive sites when diluted with a shorter chain alkanethiol. As the mole fraction of the ferrocene component increases, the voltammograms displayed broader, asymmetric peaks and finally developed a second set of peaks. This non-ideality is attributed to interactions between the ferrocene groups and the inhomogeneity of the electroactive sites at high surface concentrations. Solvation effects have also been shown to play a role in the electrochemical transformation of viologen containing monolayers in which the electroactive group is located within the hydrocarbon portion of the film at varying distances from the electrolytic solution⁶³.

Previous work by our group has shown that sulfur-based monolayers are desorbed from the electrode surface in alkaline electrolytic solutions by the application of a sufficiently negative potential³³. The surface coverage of the adsorbate is found from the charge for reductive desorption, calculated from a cyclic voltammetric scan by integrating the area under the cathodic wave, and the electron stoichiometry of the desorption reaction^{33, 52, 60}. The coverage of alkanethiolate monolayers adsorbed at gold was found to be $\sim 9.3 \times 10^{-10}$ mol/cm² based on the geometric electrode surface area and assuming a one-electron process. After accounting for the surface roughness, this value agrees with the predicted coverage of 7.6×10^{-10} mol/cm² based on the diffraction and scanning probe microscopic results discussed previously.

In spite of the large amount of research focused on organosulfur monolayers, many issues remain unresolved. Of particular importance is the interaction between the sulfur head group and the substrate. Although responsible for the formation of these films, the nature of the gold-sulfur bond is still not clear. The mechanism by which thiolate monolayers chemisorb at the surface also remains unclear along with the identity of any by-products that may be formed. Similarly, information regarding the products formed by the electrochemical cleavage of the gold-sulfur bond would increase our understanding of the reductive desorption process. On a broader topic, these organized assemblies provide a model system for studying the effect of immobilization on the reactivity of a surface-bound species.

To address these issues, we have explored the development and application of thin-layer spectroelectrochemistry for the study of sulfur-derived monolayers adsorbed at

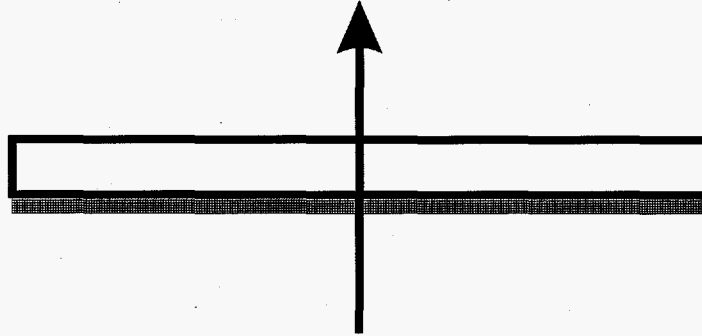
metal electrodes. The basic operating principles and advantages of this technique are described in the following section.

Thin-Layer Spectroelectrochemistry

Since the first demonstration that an optical beam passed through a transparent electrode could be used to monitor the products of an electrochemical reaction⁶⁴, spectroelectrochemistry has been widely used to investigate a variety of heterogeneous and homogeneous electrochemical processes⁶⁵⁻⁶⁸. The primary advantage is the simultaneous, in situ collection of electrochemical and spectroscopic data. The ability to monitor five independent variables (current, potential, absorbance, wavelength, and time) makes spectroelectrochemistry a versatile technique for studying interfacial phenomena.

An improvement to this technique came with the introduction of the thin-layer spectroelectrochemical cell^{67, 69}. The primary advantage of this cell is its large ratio of electrode area ($\sim 1-2 \text{ cm}^2$) to solution volume ($\sim 2-50 \text{ }\mu\text{L}$). Confining a thin solution layer ($\leq 200 \text{ }\mu\text{m}$) adjacent to the electrode surface offers several important advantages compared to the original bulk-type spectroelectrochemical cell. Electrolysis times are greatly reduced and the introduction of impurities is minimized as a result of the small volumes employed. In addition, products generated at the electrode surface are trapped within the thin solution layer and can be studied in subsequent electrochemical experiments or followed spectroscopically as a function of time without complications due to diffusion out of the optical path. Figure 2a) shows the spatial arrangement of the optical beam, electrode surface, and solution layer in this conventional thin-layer cell.

a)



Conventional Thin-Layer Cell

b)



Long Optical Pathlength Thin-Layer Cell

Figure 2. Spatial arrangement of the components in a) a conventional thin-layer cell and b) a LOPTLC.

Two drawbacks of this cell, however, are the requirement of an optically transparent electrode and the relatively low sensitivity. The low sensitivity, due to the optical pathlength being defined by the solution layer thickness, is a disadvantage for studies of weakly absorbing chromophores and/or small amounts of material such as monomolecular films.

The spatial arrangement of the components in a long optical pathlength thin-layer cell (LOPTLC), shown in Figure 2b), overcomes these two disadvantages⁷⁰⁻⁷⁴. The optical beam passes through the solution layer parallel to the electrode surface allowing electrochemical processes at solid, opaque electrodes to be investigated. Additionally, the pathlength is now dictated by the length of the solution cavity (~1 cm) rather than its thickness.

Figure 3 shows a diagram of the LOPTLC⁷² utilized for our preliminary studies of monolayer reactivity. This cell was machined from a Kel-F polymer block and has two small steps that position the electrode/substrate creating a ~100 μm -thick cavity. Quartz windows along the front and back of the cell allow the incident UV-visible beam to pass through the solution layer.

The ~100-fold sensitivity enhancement of the LOPTLC, compared to the conventional arrangement, makes it an ideal choice for investigating the reactivity of organosulfur monolayers at gold. The amount of material adsorbed or desorbed at the monolayer level is $\sim 1.5 \times 10^{-9}$ moles, assuming a surface coverage of 7.6×10^{-10} mol/cm² and an electrode area of 2 cm². However, the concentration change that results from the movement of the desorbed material into the solution layer is ~75 μM , assuming a volume

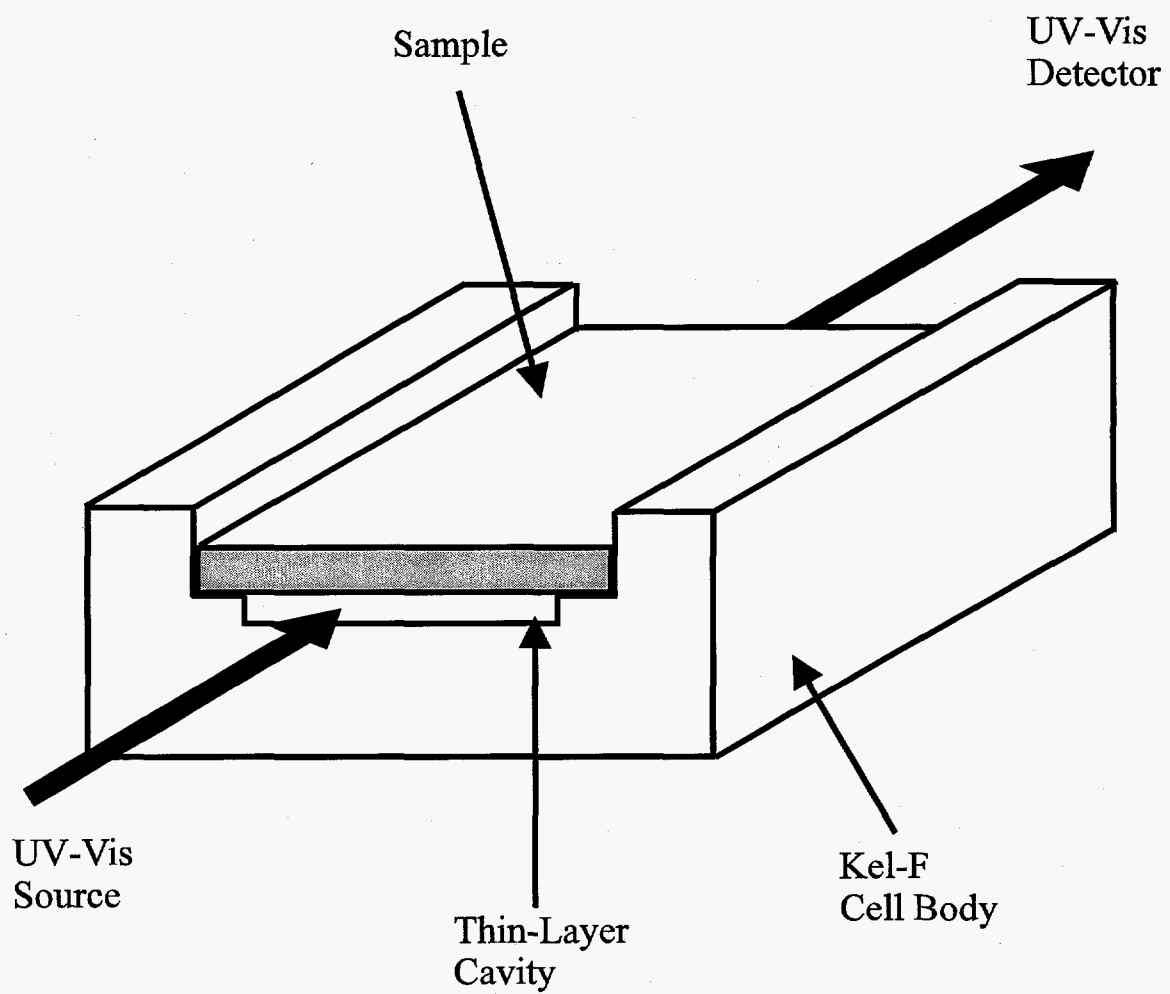


Figure 3. Diagram of an LOPTLC

of 20 μL . For a 1-cm pathlength LOPTLC and an analyte with a molar absorptivity of $1000 \text{ M}^{-1}\text{cm}^{-1}$, UV-visible spectroscopic measurements of the solution layer would detect a ~ 0.0750 absorbance unit change which is easily detectable by conventional spectrophotometers.

The chemisorption of aromatic compounds at Pt surfaces has been studied extensively using thin-layer methodology^{23, 75-78}. Even without the collection of spectroscopic data, the orientation and surface concentration were determined for 40 hydroquinone or quinone compounds. The measurement of the surface concentration of the *electro-inactive* adsorbed species is based on the disappearance of the *electroactive* precursor from solution using a multiple filling technique. The surface concentration is found from the difference in the amount of precursor remaining in solution for the first and second filling, which is determined from the reversible diphenol/quinone redox activity. The surface orientation is then deduced by comparing the average area occupied per molecule to the theoretical area calculated for various possible closest-packed orientations. The orientation has been shown to vary with precursor concentration, temperature, and the presence of competing adsorbates. At dilute precursor concentrations, most molecules were adsorbed in a flat orientation which was also confirmed by long optical pathlength thin-layer spectroelectrochemistry⁷¹.

The previous applications of thin-layer techniques to the study of adsorbed species and the sensitivity of the LOPTLC provided the motivation for this work. The goal was to develop this technique and show that this approach is feasible for probing the reactivity of immobilized molecules at monolayer and sub-monolayer levels.

Dissertation Organization

The body of this dissertation is divided into four chapters. Chapter 2 consists of a paper describing the design, construction, and characterization of a cuvette-based LOPTLC. Chapter 3 is a paper which examines the reductive desorption process using thin-layer spectroelectrochemistry to monitor and identify the desorption product. Chapter 4 is a paper describing the characterization of monolayers functionalized with a catechol terminal group which serves as a redox transformable coordination site for metal ion binding. Chapter 5 discusses the application of thin-layer spectroelectrochemistry to acid-base reactivity studies of surface-immobilized molecules. The final section provides some general conclusions and a prospectus for future studies.

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6. GENERAL CONCLUSIONS AND FUTURE PROSPECTS

This dissertation has presented several results which add to the general knowledge base regarding sulfur-derived monolayers adsorbed at gold films. Common to the body of this work is the use of thin-layer spectroelectrochemical techniques to gain insight into the chemical and electrochemical reactivity of surface-immobilized molecules.

The most prominent development from this work is the addition of a powerful technique to our group which allows the simultaneous in situ collection of both spectroscopic and electrochemical data. The cell design described herein has been optimized for use with electrodes prepared by the deposition of thin metal films onto insulating substrates making it more convenient and simple to use than its predecessor. Although the substrates examined in this work consisted entirely of gold films, this same approach can be taken with other smooth electrode/substrate materials. In addition, the ability to purge the cuvette headspace continuously with an inert gas provides an environment with a controlled oxygen level. This is vital for continued studies of the reductive desorption process

Studies of the electrochemical reductive desorption process have shown that information can be obtained regarding the structure of a chromophore-containing desorption product. Additionally, the total charge per molecule required for reductive desorption is readily obtained. Determination of this parameter provides the quantitative link necessary for surface coverage measurements based on desorption experiments in conventional electrochemical cells which have the advantage of being simpler and faster. Continued studies along this vein include the investigation of the reductive desorption of several

chromophore-containing monolayers to determine if the electron stoichiometry for other monolayers is the same as for MBA.

The ability to include a chromophore containing species in the thin solution layer that allows us to monitor a reaction of interest, as illustrated by Chapters 4 and 5, has some potentially important applications. One of the fundamental issues related to the mechanism of thiol adsorption at gold concerns the fate of the hydrogen on the sulfur head group. The utility of the cell for detecting pH changes in the solution layer may be exploited to investigate whether the by-product of thiol adsorption is a proton.

The studies described in this dissertation have primarily relied on equilibrium measurements. Future work relating to the kinetics of adsorption and desorption of thin films is now possible with the introduction of the template-stripped gold electrodes described in Chapter 3. Earlier attempts at time-based measurements were prevented by delamination of the Au/mica electrodes that were originally used.

The ability to manipulate surface architectures and control the interfacial properties of materials will continue to drive the advancement of technology. As the field of organosulfur monolayers expands and more applications are found, the answers to many of the remaining issues will require the development of additional characterization methods.