

Spectroscopic and electrochemical characterization of interfacial biomimetic assemblies on electrochemically generated gold oxide surfaces

Paweł Krysiński^{a,*}, G.J. Blanchard^b

^aLaboratory of Electrochemistry, Department of Chemistry, University of Warsaw, 02-093 Warsaw, Pasteura 1, Poland

^bDepartment of Chemistry, Michigan State University, East Lansing, MI 48824-1322, USA

Received 5 December 2003; received in revised form 24 March 2004; accepted 29 March 2004

Abstract

We report on the formation of a gold oxide layer and the reaction of this oxide with an acid chloride to form a stable, relatively complete monolayer bound through an ester-like bond to the gold oxide surface. We have used cyclic voltammetry, FTIR and optical ellipsometry to characterize this novel monolayer structure. The exposed functional groups of this monolayer can participate in subsequent surface reactions, opening the door to the use of oxide-based surface attachment chemistry on metallic substrates. This chemistry will allow for the formation of films tailored to contain both hydrophobic and hydrophilic regions, stacked at predetermined distances from the substrate that may serve as biomembrane mimetic assemblies.

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Keywords: Self-assembly; Metal oxide; Acid chloride adlayer

1. Introduction

Alkanethiol/gold self-assembled monolayers (SAMs) have assumed substantial technological importance as interfacial materials since they were first discovered in the mid-1980s [1–3]. These materials have proven to be an archetypal system for gaining fundamental insight into monomolecular interfaces and, from an applied perspective, alkanethiol/gold SAMs have found use in controlling phenomena such as wetting [4], adhesion [5] and metal deposition [6] in the fabrication of all-organic electronic circuits and the design of arrays of nanometer- and micrometer-sized structures of polymeric materials on surfaces [7–9]. Despite these very useful properties, alkanethiol/gold SAMs are limited in two respects; the chemical functionality available to create more complex layered structures using gold/sulfur attachment chemistry,

and the modest driving forces for the formation of the gold/thiol system [10,11].

To overcome these limitations, there has been extensive research into the formation of stable and well-controlled multilayer species on a variety of metal oxide and semiconductor surfaces. Over the past decade, a number of systems, including fatty acids, phosphonates and amines on oxides and organosilicon derivatives on silicon, silica and metal oxide electrodes, such as SnO₂, TiO₂, RuO₂ and ITO, have been investigated [3,5,6,12–17]. Similar chemistry, utilizing organosilicon compounds has been used extensively for modification of metallic substrates, mainly Pt, which were previously oxidized electrochemically or chemically [17].

In all of these cases, the chemistry applicable to metals has limited to silanization of oxidized metallic surfaces and this has kept a variety of interfacial structures from being applied to electrochemically active surfaces. If the rich knowledge base in oxide chemistry could be applied directly to electrochemically active surfaces, many novel device and sensor structures could be accessed.

While the formation of a gold oxide layer on electrode surfaces is well established, the long-term stability and

* Corresponding author. Tel.: +48 22 822 02 11x286; fax: +48 22 822 59 96.

E-mail address: pakrys@chem.uw.edu.pl (P. Krysiński).

reactivity of the resulting surface have yet to be examined. Previous work has demonstrated the formation of alkanethiol monolayers on oxidized gold [18–21], and for such systems, the existing oxide is sometimes viewed as an impediment to the organization and stability of alkanethiol SAMs.

We report on an efficient route to the covalent attachment of a relatively well-organized, stable monolayer to an oxidized gold surface through an ester-like bond by reaction of the metal oxide with an acid chloride. This type of surface modification technique is well established in the literature of carbon surfaces [14], yet to our knowledge has not been employed for metallic substrates. We use the electrochemically generated gold oxide film as a reactive substrate and demonstrate a monomolecular interfacial layer possessing a significant degree of organization as shown by ellipsometry, FTIR spectroscopy and electrochemistry. Initial indications are that the adlayer is bound to the gold oxide surface *at least* as strongly as alkanethiol monolayers of comparable length¹ and that this reaction appears to stabilize the underlying gold oxide. By virtue of the robust nature of the covalent surface attachment, complex interfacial structures will likely be easier to access synthetically. The chemistry we report allows for the formation of films tailored to contain both hydrophobic and hydrophilic regions, stacked at predetermined distances from the substrate, as was shown in our previous work [22,23]. Moreover, our chemistry involves neither sulfur nor silicon atoms as means of covalent attachment to the electroactive substrate, relying solely on oxygen and carbon forming ester-like bonds. These are structures that are difficult to access using alkanethiol and other methodologies, but one that will likely prove important in a variety of areas, ranging from the creation of biomimetic membrane systems compatible with the present-day microelectronic sensing and transduction devices to novel interfacial materials for chemical separations and micropatterning applications [14,24,25].

Most integral membrane proteins (e.g., ion channels and/or pumps) considered for biocatalytic or sensoric purposes require a combined hydrophobic–hydrophilic environment to retain their native structure and functions. Additionally, by virtue of the same requirements, such molecules should be decoupled from the surface of metal to avoid denaturing. Therefore, there is a great need for stable molecular matrices that functionalize electrode surface providing a biomimetic, natural environment for immobilization of biomaterial under nondenaturing conditions and in well-defined orientation. The interfacial structures we report here provide the chemical functionalities available to create more complex layered structures that can be built to accommodate

biomolecules of various hydrophobic/hydrophilic requirements, a feature difficult to achieve with metal/alkanethiol chemistry.

2. Experimental

2.1. Chemicals

All chemicals used were of the highest quality available commercially: gold, gold-covered silicon, chromic acid (VWR Scientific Products), sulfuric acid (CCI, ACS/Reagent grade), sodium sulfate (Spectrum Quality Products), ferrocenemethanol (Aldrich, 97%), adipoyl chloride (Aldrich), 4-methylmorpholine (Aldrich, 99%), dry acetonitrile (Aldrich), chloroform (Aldrich, 99.8%), ethyl acetate (Spectrum Quality Products, Inc, ACS/Reagent grade). Deionized water was available in-house.

2.2. Electrochemistry

Electrochemical measurements were made with a PC-controlled Model 650A Electrochemical Workstation (CH Instruments, USA), using a small-volume three-electrode cell with a Pt wire as counter electrode. All potentials are quoted vs. a Ag/AgCl/1M KCl_{aq} reference electrode.

2.3. IR and IRRAS spectroscopy

For monolayer self-assembly on gold-plated silicon slides, infrared reflection–absorption spectra (IRRAS) were acquired with 4 cm^{−1} resolution using a Nicolet Magna 750 FTIR spectrometer. The external reflectance sample mount was set to an incidence angle of 80° with respect to the substrate normal. Transmission IR spectra were collected with 4 cm^{−1} spectral resolution in a Nicolet Magna 550 FTIR spectrometer.

2.4. Optical ellipsometry

Ellipsometric thickness measurements of adlayers formed on the electrochemically oxidized gold surface were made with a Rudolph Auto-EL II optical null ellipsometer, operating at 632.8 nm. Rudolph DAFIBM software was used for data collection and processing.

2.5. Preparation of gold substrates and oxide layer formation

Gold substrates for electrochemical measurements (Au, 99.99%, 0.5 mm diameter wire with tip melted to form a gold-ball electrode; electrochemical area 0.16 cm² (determined by cyclic voltammetry using the kinetically reversible K₄Fe(CN)₆/K₃Fe(CN)₆ redox probe [11]) were cleaned by annealing in a reductive flame, then polarized cyclically (scan rate 0.1 V/s) in the −0.3 to 1.5 V potential range in 0.5

¹ For the comparison to be made accurately, we consider that the attractive interchain interactions, which are important for alkanethiol SAMs, may also be important to the adlayer organization for the monolayer we report here.

M H_2SO_4 (aq) solution. The electrodes were then cycled with the same rate in 0.5 M Na_2SO_4 (aq) solution in the potential window of -0.4 to 1.2 V. Once reproducible voltammograms were obtained (Fig. 1), the potential cycle was stopped at 1.2 V for 60 s and, under potential control, the electrodes were removed from the cell, washed with distilled water and dried with a stream of nitrogen. These reproducible cyclic voltammograms were also used to evaluate the “real” electrode area from the reduction of gold oxide by the method of Hoogvliet et al. [26] and the conversion factor of 0.48 mC/cm^2 [27]. Using this information, we can estimate a roughness factor of 1.1 ± 0.03 for our gold-ball electrodes [26,35]. For estimation of electrochemically generated gold oxide thickness and electrode coverage by the adipoyl chloride adlayer, we relied solely on the experimentally determined electrochemical electrode area, without using a surface roughness factor. In our opinion, the formation of a thicker oxide layer, after stopping the potential at 1.2 V for 60 s, changes the roughness factor of such treated gold surface.

Planar gold substrates were made from silicon wafers, $A=2 \text{ cm}^2$, with evaporated gold (1000 \AA) deposited on a

chromium adhesion layer. The gold-coated substrates were cleaned by immersion in hot chromic acid (95°C , 30 s) and rinsed with distilled water. The clean substrates were transferred to the electrochemical cell and polarized cyclically in 0.5 M Na_2SO_4 (aq), the same as was done with the gold-ball electrodes. Polarization in acidic media between -0.3 and 1.5 V was omitted to avoid dissolution of the chromium layer and delamination of the gold layer. This procedure resulted in a stable open circuit potential for both types of the substrate of ca. 0.76 V , characteristic of the formation of a hydrated oxide layer on gold.

3. Results and discussion

The focus of this work is on a novel strategy of molecular self-assembly which allows a variety of surfaces, ranging from metals to semiconductors and oxides, to be treated using the same layer growth chemistry. We report on the electrochemical growth and characterization of the interfaces using cyclic voltammetry, FTIR spectroscopy and optical ellipsometry.

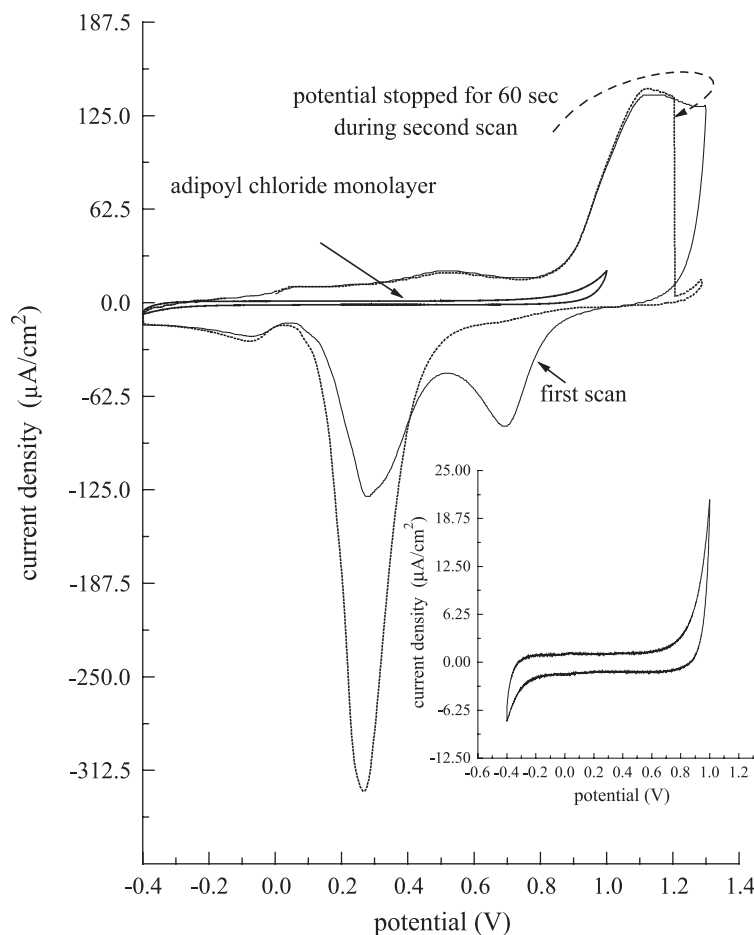
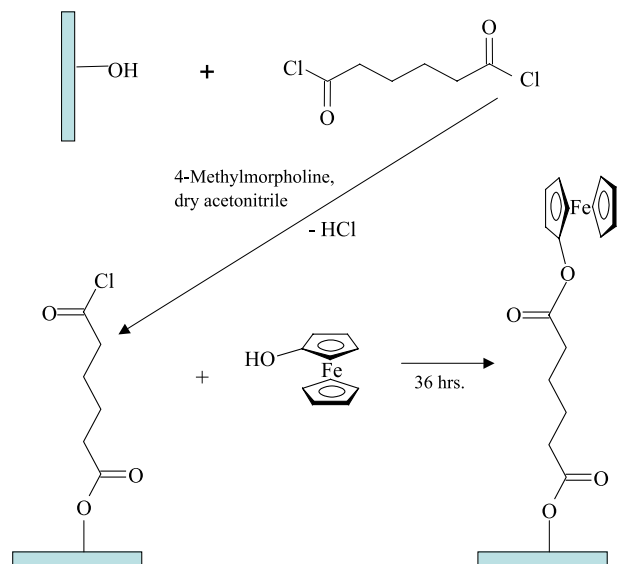


Fig. 1. Cyclic voltammogram of bare gold, first cycle (thin solid line), bare gold following 60 s at 1.2 V to form the oxide layer (dotted line) and after reaction of the oxide layer with adipoyl chloride (thick solid line) in aqueous $0.5 \text{ M Na}_2\text{SO}_4$ solution. Inset: enlarged view of CV for adlayer. Scan rate for all cases: 0.1 V/s .



Scheme 1. Adipoyl adlayer formation and attachment of ferrocenemethanol to adlayer terminal acid chloride group.

As is well established in the literature, the electrochemistry of gold in aqueous media involves double layer charging/discharging phenomena, a preoxidation region, monolayer gold oxide (or hydroxide) formation and after going to more positive potentials, bulk oxide formation [28–30]. Gold anodic oxidation yields a Au(III) hydroxide surface layer consisting of 2.5 to 3 molecular layers of hydrated $\text{Au}(\text{OH})_3$ [31–33]. There is extensive literature evidence for the relative stability of the gold oxide layer, which can be formed in various potential windows, depending on pH and solution composition [26,34,35]. The electrochemical formation of the oxide (or hydroxide) of gold is typically performed in acidic media and the equilibrium potential of this reaction is 1.28 V vs. SHE [33].

In this work, we kept the potential polarization window in the range of the formation of a monolayer of oxidized gold, without producing bulk gold oxide. However, the charge resulting from a 60-s polarization of the electrode at 1.2 V to produce the $\text{Au}(\text{OH})_3$ (s) that was determined by integration of the gold oxide cathodic peak (Fig. 1, dotted trace) at ca. 0.26 V (vs. Ag, AgCl|1 M KCl_{aq}) yielded a value approximately twice that for the anodic peak observed under continuous cycling conditions. We infer from these data that the oxide layer we form is more than one layer thick, consisting of hydrated $\text{Au}(\text{OH})_3$, a result consistent with the literature on anodic oxidation [31–33] and XPS data [19,20,28,36]. We cannot be more quantitative, however, because the thickness change in the layer is likely accompanied by a change in the surface roughness factor. We reacted the oxide layer with adipoyl chloride in dry acetonitrile, using 4-methylmorpholine as a Lewis base (50:1:1) under nitrogen for ~12 h. The reacted substrates were removed and rinsed with ethyl acetate. Cyclic voltammetry of the gold ball electrode after reaction of the surface oxide with adipoyl chloride (Fig. 1 inset) reveals a

substantial change compared to that seen for bare gold under the same experimental conditions. These data indicate the formation of an adlayer on the gold oxide surface. It is important to note that the CV curve, shown in the inset of Fig. 1, remains stable in continuous cycling, showing that regardless of inherent instability of gold oxide, the presence of the adipoyl chloride adlayer stabilizes the underlying, electrochemically generated gold oxide.

Gold-plated silicon slides were then dried under a stream of nitrogen and used for IRRAS measurements. Ellipsometric data averaged over 40 measurements on eight individual samples yielded a film thickness of 8.5 ± 1.5 Å, consistent with the addition of a single layer of adipoyl chloride. To characterize the resulting adlayer packing density, the acid chloride terminal functionality was reacted with ferrocenemethanol (Scheme 1). Gold ball electrodes were exposed to 10 ml 0.5 mM ferrocenemethanol in dry acetonitrile with 0.1 ml 4-methylmorpholine under nitrogen for ~36 h.

The cyclic voltammetry of the ferrocene/ferrocenium redox centers was then followed to evaluate the surface coverage of the gold substrates (Fig. 2). The insert shows the voltammetric peak current dependence of the scan rate, which is linear over the potential scan rate range studied here, indicating that the redox couple is surface-bound.

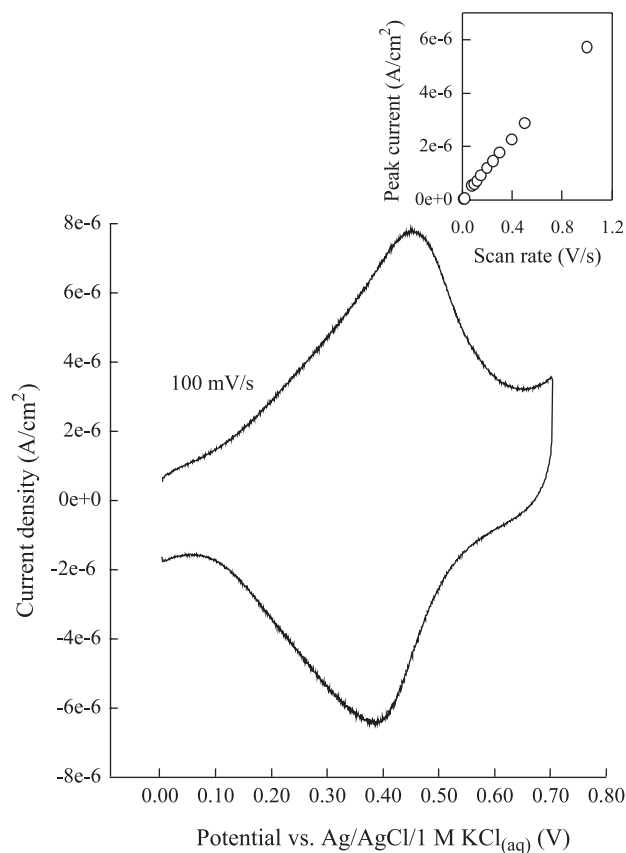


Fig. 2. Cyclic voltammogram of iron ferrocene-modified surface in 0.1 M HClO_4 aq, 100 mV/s scan rate. Inset: Dependence of peak current on scan rate.

Integration of the surface charge (the electrochemical area of electrode was used, which is likely more appropriate than geometric estimations based on the sphere radius [37,40,43]) of ferrocene oxidation (or reduction of the ferrocenium species yields a surface coverage of 1.5×10^{-10} mol cm⁻², somewhat lower than that expected for monolayer coverage (4×10^{-10} mol cm⁻²) [38–41] and ca. five times smaller than the density reported for an alkanethiol monolayer (7.7×10^{-10} mol cm⁻²) [42]. There are other literature reports, however, which indicate a lower surface loading [43], so our findings are well within the expected range of coverage. We believe that only a fraction of the adipoyl chloride molecules bound to the gold oxide surface react with ferrocenemethanol, either for steric reasons or because the two COCl terminations of the same adipoyl chloride molecule may bind with the surface. Moreover, we cannot exclude that only part of the surface hydrous oxide reacted with adipoyl chloride. Therefore, the electrochemical surface coverage may represent a lower limit for the amount of adipoyl chloride on the gold oxide surface. Similar or even smaller coverage reported in our earlier work on gold and on ITO [23,44] enabled us to form hybrid bilayers with an external leaflet made out of phospholipids, proving the feasibility of such systems in biomimetics. Further studies are under way to determine other factors that can affect the adlayer density and organization. Our focus in these studies will be on the influence of surface roughness and the structure of the adlayer constituents.

The spectroscopic data (Fig. 3) confirm the formation of an adlayer on the oxidized gold surface. These spectra reveal a significant difference between bulk adipoyl chloride and the same moiety bound to a gold oxide surface. The acid chloride C=O peak seen in the bulk at 1793 cm⁻¹ disappears coincident with the appearance of an ester C=O resonance at 1740 cm⁻¹ for the adlayer [45,46]. In addition, the appearance of a small peak at 1814 cm⁻¹ may be indicative of a terminal acid chloride functionality [46]. The bands in the 1400–1500 cm⁻¹ region of the adlayer spectrum (Fig. 3b) are associated with the symmetric and asymmetric stretches of a terminal carboxylate functionality. Their intensity increases in time under ambient conditions (spectrum not shown). These findings indicate a gradual hydrolysis of the terminal acid chloride moiety subsequent to adlayer formation, and this is not a surprising result, since—as stated before—the spectroscopic data were taken under ambient conditions. The IR spectrum also contains C–O–Au ester-like stretches in 1167 cm⁻¹ and at 1260 cm⁻¹. The correspondence of these bands with those of an ester suggests that the Au–O bond is of substantially the same strength as a normal ester C–O bond [45]. We note the presence of a broad band in the 2000–2100 cm⁻¹ region in the adlayer spectrum (Fig. 3a). This band and the sharp peak in the region of 3700 cm⁻¹ are seen in all adlayer spectra and there are relatively few functionalities that are characterized by resonances at this energy. The 2000–2100 cm⁻¹ band may be due to the

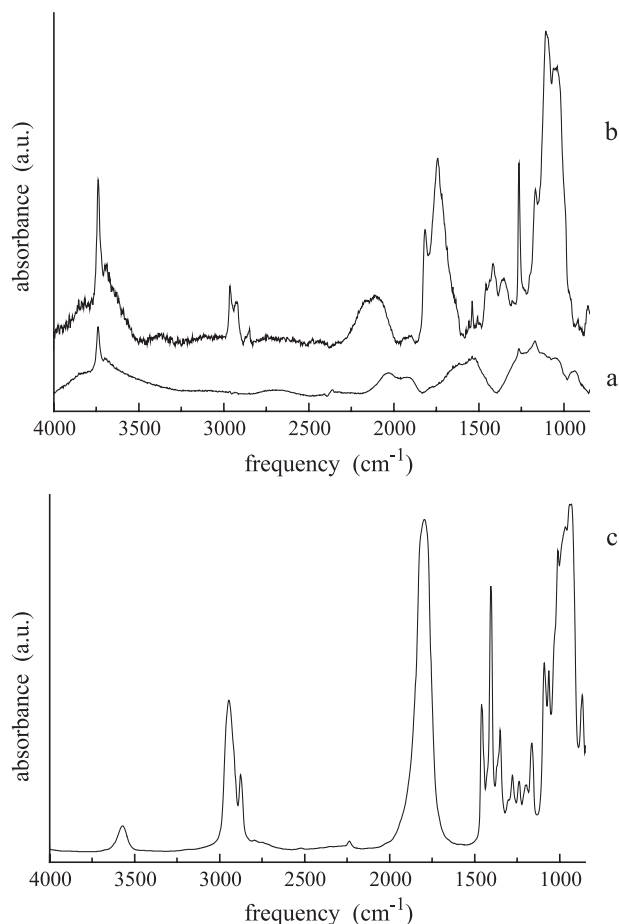


Fig. 3. (a) FTIR spectrum of gold oxide adlayer on a metallic gold substrate. (b) FTIR spectrum of an adipoyl chloride monolayer bound to gold oxide. (c) FTIR spectrum of bulk adipoyl chloride.

presence of surface-bound OH functionalities on the oxidized gold substrate, interconnected via hydrogen bonds or non-stoichiometric water associated with them. The band around 3700 cm⁻¹ can be related to similar functionalities with no hydrogen bonds between them. Further investigation will be required to assign these bands unambiguously.

4. Conclusions

We present a new means of self-assembly that opens up possibilities for the modification of variety of surfaces, including metal, oxide and semiconductor surfaces. This approach expands the range of chemical reactions and thus molecular structure available for surface functionalization. Our experimental data show that we can bond a monolayer of an acid chloride to an electrochemically oxidized gold surface through the ester-like linkage. Monolayer surface coverage, estimated with the use of ferrocene redox centers bound covalently to the monolayer, is at least 1.5×10^{-10} mol cm⁻². We are using this surface attachment chemistry to investigate the lifetime and dynamics of fluorophores

bound within layered structures on ITO, quartz and gold surfaces [22,23]. Our initial work shows that, despite the well-known inherent instability of gold oxide, the electrochemical window of stability for the film in oxygen-containing aqueous media is limited cathodically by hydrogen peroxide formation at gold (ca. -0.2 V) and can easily be extended to -0.4 V in deaerated solution (Fig. 1 inset). The stabilizing effect we observe for the Au–O bond is likely due to the formation of ester functionalities from the gold oxygen species at the interface, as well as possible interactions between neighboring ester carbonyl functionalities. The anodic scan of the adlayer (Fig. 1 inset) is apparently limited by the electrochemical oxidation of gold generating more oxide, which changes the structure of the interface. However, simultaneous oxidative desorption of the adipoyl chloride monolayer cannot be excluded. Further studies involving adlayer molecules with longer aliphatic chains will be required to improve the insulating behavior of these oxide-bound films and evaluate the extent of their organization. One substantial opportunity for this family of films lies in their use as matrices capable of incorporating biomimetic sensing elements or biocatalysts in systems that are electronically and mechanically compatible with present sensor technology [14,22–24]. The interfacial bonding motif we report here is characterized by a hydrophilic region close to the electrode surface. Both the gold oxide involved in the formation of the ester-like bond to the adlayer and the adlayer moiety can be tailored with respect to their structure and thickness using appropriate chemistry. The presence of the reactive acid chloride terminal functionality provides an efficient and robust means for binding a variety of species, such as bimolecular membranes, to the substrate. Such a structural motif would potentially be superior to hybrid alkanethiol/lipid films owing to the strength of the covalent bond to the interface.

Acknowledgements

We are grateful to the U. S. Department of Energy for support of this work under grant DEFG0299ER15001 and to NATO under grant PST.CLG.977966. We thank Prof. Jolanta Bukowska, Laboratory of Molecular Interactions, Department of Electrochemistry, Warsaw University, Warsaw, Poland, for valuable discussions of the IR data.

References

- [1] A. Ulman, Formation and structure of self-assembled monolayers, *Chem. Rev.* 96 (1996) 1533–1554.
- [2] H.O. Finklea, Electrochemistry of organized monolayers of thiols and related molecules on electrodes, in: A.J. Bard, I. Rubinstein (Eds.), *Electroanal. Chem.: A Series of Advances*, vol. 19, Marcel Dekker, New York, 1996, pp. 109–335.
- [3] D.L. Allara, R.G. Nuzzo, Spontaneously organized molecular assemblies: 1. Formation, dynamics, and physical properties of n-alkanolic acids adsorbed from solution on an oxidized aluminum surface, *Langmuir* 1 (1985) 45–52.
- [4] G.M. Whitesides, P.E. Laibinis, Wet chemical approaches to the characterization of organic surfaces: self-assembled monolayers, wetting, and the physical-organic chemistry of the solid–liquid interface, *Langmuir* 6 (1990) 87–96.
- [5] G.P. Lopez, M.W. Albers, S.L. Schreiber, R.N. Carroll, E. Peralta, G.M. Whitesides, Convenient methods for patterning the adhesion of mammalian cells to surfaces using self-assembled monolayers of alkanethiols on gold, *J. Am. Chem. Soc.* 115 (1993) 5877–5878.
- [6] W.P. Wuelfing, F.P. Zamborini, A.C. Templeton, X.G. Wen, H. Yoon, R.W. Murray, Monolayer-protected clusters: molecular precursors to metal films, *Chem. Mater.* 13 (2001) 87–95.
- [7] L.F. Rozsnyai, M.S. Wrighton, Selective electrochemical deposition of polyaniline via photopatterning of a monolayer-modified substrate, *J. Am. Chem. Soc.* 116 (1994) 5993–5994.
- [8] Z. Huang, P.-C. Wang, A.G. MacDiarmid, Y. Xia, G.M. Whitesides, Selective deposition of conducting polymers on hydroxyl-terminated surfaces with printed monolayers of alkylsiloxanes as templates, *Langmuir* 13 (1997) 6480–6484.
- [9] W.A. Hayes, H. Kim, X. Yue, S.S. Perry, C. Shannon, Nanometer-scale patterning of surfaces using self-assembly chemistry: 2. Preparation, characterization, and electrochemical behavior of two-component organothiol monolayers on gold surfaces, *Langmuir* 13 (1997) 2511–2518.
- [10] D.S. Karpovich, G.J. Blanchard, Direct measurement of the adsorption kinetics of alkanethiolate self-assembled monolayers on a microcrystalline gold surface, *Langmuir* 10 (1994) 3315–3323; H.M. Schessler, D.S. Karpovich, G.J. Blanchard, Quantitating the balance between enthalpic and entropic forces in alkanethiol/gold monolayer self assembly, *J. Am. Chem. Soc.* 118 (1996) 9645–9651.
- [11] P. Krysiński, M. Brzostowska-Smolka, Three-probe voltammetric characterisation of octadecanethiol self-assembled monolayer integrity on gold electrodes, *J. Electroanal. Chem.* 424 (1997) 61–67.
- [12] W.A. Hayes, C. Shannon, Nanometer-scale patterning of surfaces using self-assembly chemistry: 3. Template-directed growth of polymer nanostructures on organothiol self-assembled mixed monolayers, *Langmuir* 14 (1998) 1099–1102.
- [13] J. Sagiv, Organized monolayers by adsorption: 1. Formation and structure of oleophobic mixed monolayers on solid surfaces, *J. Am. Chem. Soc.* 102 (1980) 92–98.
- [14] I. Willner, E. Katz, Integration of layered redox proteins and conductive supports for bioelectronic applications, *Angew. Chem. Int. Ed.* 39 (2000) 1180–1218.
- [15] J. Facci, R.W. Murray, Silanization and non-aqueous electrochemistry of two oxide states on platinum electrodes, *J. Electroanal. Chem.* 112 (1980) 221–229.
- [16] L.D. Burke, M.B.C. Roche, Hydrous oxide formation on platinum—a useful route to controlled platinization, *J. Electroanal. Chem.* 164 (1984) 315–334.
- [17] J.R. Lenhard, R.W. Murray, Chemically modified electrodes: 13. Monolayer/multilayer coverage, decay kinetics, and solvent and interaction effects for ferrocenes covalently linked to platinum electrodes, *J. Am. Chem. Soc.* 100 (1978) 7870–7875.
- [18] H. Ron, S. Matlis, I. Rubinstein, Self-assembled monolayers on oxidized metals: 2. Gold surface oxidative pretreatment, monolayer properties, and depression formation, *Langmuir* 14 (1998) 1116–1121.
- [19] C. Yan, A. Götzhäuser, M. Grunze, Ch. Wöll, Formation of alkanethiolate self-assembled monolayers on oxidized gold surfaces, *Langmuir* 15 (1999) 2414–2419.
- [20] J.T. Woodward, M.L. Walker, C.L. Meuse, D.J. Vanderah, G.E. Poirier, A.L. Plant, Effect of an oxidized gold substrate on alkanethiol self-assembly, *Langmuir* 16 (2000) 5347–5353.
- [21] H. Ron, I. Rubinstein, Alkanethiol monolayers on preoxidized gold. Encapsulation of gold oxide under an organic monolayer, *Langmuir* 10 (1994) 4566–4573.

- [22] L. Kelepouris, P. Krysiński, G.J. Blanchard, Gauging molecular interactions between substrates and adsorbates. Substrate mediation of surface-bound chromophore vibronic coupling, *J. Phys. Chem., B* 107 (2003) 4100–4106.
- [23] P. Krysiński, G.J. Blanchard, Synthesis and characterization of amphiphilic biomimetic assemblies at electrochemically active surfaces, *Langmuir* 19 (2003) 3875–3882.
- [24] E.-K. Sinner, W. Knoll, Functional tethered membranes, *Curr. Opin. Chem. Biol.* 5 (2001) 705–711.
- [25] R. Guidelli, G. Aloisi, L. Becucci, A. Dolfi, M.R. Moncelli, F.T. Buoninsegni, Bioelectrochemistry at metal/water interfaces, *J. Electroanal. Chem.* 504 (2001) 1–28.
- [26] J.C. Hoogvliet, M. Dijkema, B. Kamp, W.P. van Bennekomp, *Anal. Chem.* 72 (2000) 2016–2021; M. Dijkema, B. Kamp, J.C. Hoogvliet, W.P. van Bennekomp, Formation and electrochemical characterization of self-assembled monolayers of thioctic acid on polycrystalline gold electrodes in phosphate buffer pH 7.4, *Langmuir* 16 (2000) 3852–3857.
- [27] W. Yang, J.J. Gooding, D.B. Hibbert, Characterisation of gold electrodes modified with self-assembled monolayers of l-cysteine for the adsorptive stripping analysis of copper, *J. Electroanal. Chem.* 516 (2001) 10–16.
- [28] L.D. Burke, D.T. Buckley, J.A. Morrissey, Novel view of the electrochemistry of gold, *The Analyst* 119 (1994) 841–845.
- [29] P. Hale, S. Thurgate, P. Wilkie, Structural changes during oxidation of Au(110), *Surf. Interface Anal.* 32 (2001) 240–244.
- [30] L.D. Burke, P.F. Nugent, Multicomponent hydrous oxide films grown on gold in acid solution, *J. Electroanal. Chem.* 444 (1998) 19–29.
- [31] K. Juodkazis, J. Juodkazyte, V. Jasulaitiene, A. Lukinskas, B. Sebek, XPS studies on the gold oxide surface layer formation, *Electrochem. Commun.* 2 (2000) 503–507.
- [32] K. Juodkazis, J. Juodkazyte, T. Juodiene, A. Lukinskas, Determination of Au(III) in the surface layers formed anodically on the gold electrode, *J. Electroanal. Chem.* 441 (1998) 19–24.
- [33] K. Juodkazis, J. Juodkazyte, B. Sebek, A. Lukinskas, Cyclic voltammetric studies on the reduction of a gold oxide surface layer, *Electrochem. Commun.* 1 (1999) 315–318.
- [34] A. Tymosiak-Zielinska, Z. Borkowska, Interfacial properties of polycrystalline gold electrodes in tetraalkylammonium electrolytes, *Electrochim. Acta* 46 (2001) 3073–3082.
- [35] R. Słojkowska, M. Jurkiewicz-Herbich, Adsorption study of amino acids on a polycrystalline gold electrode, *Colloids Surf., A* 178 (2001) 325–336.
- [36] A. Krozer, M. Rodahl, X-ray photoemission spectroscopy study of UV/ozone oxidation of Au under ultrahigh vacuum conditions, *J. Vac. Sci. Technol., A* 15 (1997) 1704–1709.
- [37] J.J. Sumner, S.E. Creager, Redox kinetics in monolayers on electrodes: electron transfer is sluggish for ferrocene groups buried within the monolayer interior, *J. Phys. Chem., B* 105 (2001) 8739–8745.
- [38] J.Y. Gui, D.A. Stern, F. Lu, A.T. Hubbard, Surface chemistry of five-membered heteroaromatics at Pt (111) electrodes studied by EELS, LEED, Auger spectroscopy and electrochemistry: furan, pyrrole and thiophene, *J. Electroanal. Chem.* 305 (1991) 37–55.
- [39] G. Zotti, G. Schiavon, S. Zecchin, A. Berlin, G. Pagani, Adsorption of ferrocene compounds on indium-tin-oxide electrodes. Enhancement of adsorption by decomposition of ferrocenium molecules by oxygen, *Langmuir* 14 (1998) 1728–1733.
- [40] J.J. Sumner, S.E. Creager, Topological effects in bridge-mediated electron transfer between redox molecules and metal electrodes, *J. Am. Chem. Soc.* 122 (2000) 11914–11920.
- [41] C.E.D. Chidsey, C.R. Bertozzi, T.M. Putvinski, A.M. Majsce, Coadsorption of ferrocene-terminated and unsubstituted alkanethiols on gold: electroactive self-assembled monolayers, *J. Am. Chem. Soc.* 112 (1990) 4301–4306.
- [42] S. Kuwabata, R. Fukuzaki, M. Nishizawa, C.R. Martin, H. Yoneyama, Electrochemical formation of a polyaniline-analogue monolayer on a gold electrode, *Langmuir* 15 (1999) 6807–6812.
- [43] J.J. Sumner, K.S. Weber, L.A. Hockett, S.E. Creager, Long-range heterogeneous electron transfer between ferrocene and gold mediated by *n*-alkane and *N*-alkyl-carboxamide bridges, *J. Phys. Chem., B* 104 (2000) 7449–7454.
- [44] M. Mazur, G.J. Blanchard, Photochemical and electrochemical oxidation reactions of surface-bound polycyclic aromatic hydrocarbons, *J. Phys. Chem., B* 108 (2004) 1038–1045.
- [45] J. Dai, A.W. Jensen, D.K. Mohanty, J. Erndt, M.L. Bruening, Controlling the permeability of multilayered polyelectrolyte films through derivatization, cross-linking, and hydrolysis, *Langmuir* 17 (2001) 931–937.
- [46] R.M. Silverstein, G.C. Bassler, C.T. Morrill, *Spectrometric Identification of Organic Compounds*, 5th ed., Wiley, New York, 1991, pp. 114–121.