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Oxidative desorption of thiols as a route to controlled formation of binary self assembled monolayer surfaces

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ABSTRACT

Binary self-assembled monolayers have been prepared by an alternative route to the conventional approach where a surface is exposed to a solution of both thiols at open circuit. A particular composition can be prepared with relative ease and the method is particularly useful for binary monolayers comprising two thiols with very different chain lengths since the problem of the longer chain thiol displacing the shorter over time is avoided. This is achieved by first preparing a full monolayer of the longer thiol, then oxidative desorption is carried out using cyclic voltammetry to remove a known fraction (as measured from the charge associated with gold oxide reduction) of the original SAM. Experiments with several thiols of chain lengths from 9 to 16 carbon atoms show that a considerable degree of control may be exerted over the rate at which the thiol is removed, using factors such as the potential limit, scan rate, pH and electrolyte polarity. The amount of thiol removed can thus also be controlled in a similar fashion. Once the oxidative desorption has taken place to the required degree, the vacancies created can be filled by exposure to a solution of a second thiol, differing in either chain length, termination or both. Deposition of thiols was carried out both under potential control (for longer chains) and by simple adsorption (for shorter chains). Several binary SAMs were prepared using this method and characterised using simple cyclic voltammetry with redox probes and selective reductive desorption. This method of preparation of binary SAMS may provide an alternative to both conventional methods using solution exposure and to methods that employ reductive desorption to expose selected facets on a polycrystalline surface. It may also be used to create partially blocked electrodes.

1. Introduction

Self-assembled monolayers (SAMs) based on thiol surfactants have been the subject of intensive study for many years primarily because of the flexibility they offer for the preparation of a surface having specific chemical or physical properties by virtue of the ability to tailor the chain length and properties and to employ different functional groups at the solution-facing chain terminus. Several excellent early reviews [1–3] provide a thorough introduction to the field while a more recent review [4] shows the development of the understanding and applications of SAMs. Despite the volume of published work on the subject, new insights into factors affecting the formation and stability of SAM layers are still being discovered, for example two papers in recent years have highlighted the importance of reactant mass transfer in the formation of layers with reproducible properties [5] and the fact that the amine terminal group, often used as a reactive site, is not stable under ambient conditions because of photodegradation [6]. Reactive terminal groups are of great interest because they can serve as points of attachment for a range of molecules to be used for recognition or sensing purposes (the use of SAMS for biosensors has been reviewed in several articles [7,8]) while other species such as porphyrins, for example, have been attached to SAM monolayers widening the range of potential applications still further to areas such as electrocatalysis and molecular electronics [9]. In the area of surface attachment and sensing, the preparation of binary SAMs where the monolayer consists of two different thiols is of substantial interest. In such systems a second, non-reactive terminal group dilutes reactive sites at the interface. This is often useful since the molecules attached to a SAM for sensing, recognition or other purposes are often much larger than the SAM molecules themselves. Initial studies of binary SAMs used simple immersion of a gold substrate in a solution containing two thiols (with either differing terminal groups [10] or differing chain lengths [11]) and revealed that the composition of the resulting SAM does not necessarily reflect the composition of the thiol solution used to prepare the binary SAM. For example, it is accepted that longer chain thiols will replace shorter chain thiols over time [10,11] as layers of longer chain thiols are more stable due to increased inter-chain interactions. This means that preparation of binary SAMs of a specific composition can be difficult. Ma

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and Lennox [12] studied the variation of the open circuit potential of a gold substrate during SAM formation and then showed that layer formation at a fixed potential not only resulted in more rapid formation of excellent blocking C_{16} SAMs but also was able to exert an improved degree of control over the composition of a binary SAM of $HSC_{15}CO_2H$ and $C_{16}SH$ resulting in layers quite different in composition to those formed at open circuit by simple adsorption from a solution of the two thiols. Potential control has been used in a second approach to the formation of binary SAMs through the use of reductive desorption of part of a homogeneous monolayer to create vacancies that may subsequently be filled by a second thiol. For example, layers of mercaptopropionic acid (MPA) show several reductive desorption peaks attributed to the removal of the layer from different facets on polycrystalline gold [13]. Control of a potential scan allows the removal of MPA from Au (1 1 1) facets only and the vacant sites thus created may be filled with a second (in this case longer chain) thiol to create a mixed monolayer, or left vacant to leave a partially blocked electrode. Lemay and Shepherd [14] and Smith et al. [15] have developed this further with a pulsed desorption method to remove 2-aminoethane thiol from selective facets on gold and then prepared a heterogeneous mixed monolayer by filling the vacancies with 11-mercaptoundecanoic acid. Lee and Lennox [16] also demonstrated the ability to fill vacancies created by reductive desorption when they used a ferrocene-terminated thiol to fill vacancies and to act as a probe to examine the reductive desorption process and to identify phase-separated and mixed states in the layer.

In this paper we adopt an alternative approach to the preparation of binary SAMS of a composition that is known and can be varied with reasonable control by employing *oxidative* desorption to remove part of a monolayer. Such a method was reported previously by Chen et al. [17] who used different constant potentials to remove mercaptoacetic acid (MAA) and to fill the vacancies created with 1-dodecanethiol (DT). Their supplementary material also reported using the same strategy (but with a higher constant potential) to remove part of a DT layer and fill the vacancies with MAA. Here we have developed a variant of this system using cyclic voltammetry to gain fine control over the amount of the first thiol removed (through changes in upper scan limit, scan rate, and solution conditions) and also to monitor the change in coverage with reasonable accuracy through the use of the charge for reduction of gold oxide on sites where thiols have been removed. This method facilitates the preparation of binary monolayers of widely variable and controlled composition. In addition this work has a primary focus on the preparation of binary monolayers by filling gaps in long chain thiol layers with much shorter thiols and several binary monolayers of different compositions were prepared successfully by this method to demonstrate the broad applicability of the method.

2. Experimental

2.1. Chemicals

The thiols employed, 3-mercaptopropionic acid (MPA, 99 + % Aldrich) 16-mercaptohexadecanoic acid (Aldrich > 90%), 1-hexadecanethiol (Fluka > 95%), and nonanethiol (Aldrich 98%), were used as received. Other chemicals were AnalaR or better purity and also used as received including, $LiClO_4$, NaI, C_2H_5OH, H_2SO_4, NaOH, $K_3Fe(CN)_6$, and $Ru(NH_3)_6Cl_3$ (>98% Aldrich). Thiol solutions (5 mM), for use in potential-assisted deposition were prepared with lithium perchlorate (0.1 M) with absolute ethanol as solvent. Aqueous solutions were prepared with ultrapure water (18 MΩ cm) from a Millipore Direct Q3 UV system (Millipore).

2.2. Instrumentation and electrochemical experiments

For electrochemical experiments, a conventional 3-electrode cell was employed with a Saturated Calomel Electrode (SCE, to which all potentials are referred) and a Pt wire serving as the reference and counter electrodes, respectively. The working electrodes were polycrystalline gold discs of diameter 1.6 mm sealed in a Teflon insulating mantle (Bioanalytical Systems). The main cell was separated from the reference electrode by means of a Luggin capillary bridge, which was filled with the background electrolyte used in the relevant experiment. The potentiostat used was a BAS 100B/W (Bioanalytical Systems). Electrodes were polished with a simple slurry of alumina (0.1 μm) and then rinsed and subjected to electrochemical cleaning in 0.1 M H_2SO_4 (repeated cycling (50 mV s^{-1}) of the electrode between the system's oxygen and hydrogen evolution potentials until a reproducible voltammogram with well-defined features was obtained). The area of the electrode was determined by integrating the oxide reduction charge when the potential is reversed just before oxygen evolution at the Burshtein minimum [18]. This technique assumes that complete monolayer coverage is obtained at this potential (at a scan rate of 50 mV s^{-1}) and that this monolayer is associated with a charge of 400 μC cm^{-2} [19,20]. This conversion factor was then used to establish the area of gold freed from thiol by oxidative desorption. Some preliminary reductive desorption experiments for MPA revealed poor quality responses when compared to the literature [13] and so the gold electrodes were electropolished by cycling between −0.2 and 1.6 V for up to 60 cycles at 20 mV s^{-1} in a solution of 0.1 M $NaNO_3$ containing 1 mM KI. The electrode was then cleaned in sulphuric acid as described above, the cleaning procedure always being halted at potentials negative of gold oxide reduction in order to ensure a properly reduced gold surface. This led to an improved reductive desorption profile for MPA and as such was repeated as needed throughout the course of the work. Thiol monolayers were mainly prepared under potential control with a clean gold disc electrode being immersed in a dilute thiol solution (5 mM/0.1 M $LiClO_4$/EtOH) held at a modest positive potential (0.6 V) for 30 min whilst the electrolyte was continuously purged with nitrogen gas. When this potential was used for short chain thiols, a low but consistent oxidation current was observed, thought to be associated with the oxidation of the short chain thiol and consistent with similar observations made by Chen et al. [17]. As a consequence, simple adsorption at the open circuit potential was used when necessary to avoid the oxidation of the shorter chain thiol.

Experiments with redox probes were carried out in a solution of the electrolyte and probe using either $Fe(CN)_6{}^{3+}$ or $Ru(NH_3)_6{}^{3+}$ with specific details of solutions noted in the text and legends.

3. Results and discussion

3.1. Oxidative desorption of thiol monolayers – cyclic voltammetry

The first stage of the preparation of a binary SAM is the preparation of a full monolayer of one thiol, followed by oxidative desorption and so we first report on the oxidative desorption process. Studies of the stability of thiol monolayers as a function of potential (primarily, but not exclusively an exploration of the reductive and oxidative desorption processes) have shown a much greater emphasis on reductive desorption because it is simpler (a one electron transfer leading to the thiolate) than its oxidative equivalent (which can involve multiple electron transfer and lead to a range of products). Oxidative desorption also has the disadvantage of being complicated by the presence of gold oxide formation in the same potential region. In all, three different