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In situ Real Time Electrochemical Measurement of Kinetics of Thiol Adsorption on Gold using Microelectrode

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The growth kinetics of a self-assembled monolayer (SAM) in solution was measured *in situ* in real time electrochemistry using microelectrode. The steady-state current produced by the oxidation of ferrocene in the presence of a microelectrode was recorded as a function of time. Introduction of 11-mercaptoundecanoic acid (MUA) into the electrochemical cell produced a decrease in the steady-state current related to formation of an insulating MUA SAM. The current decrease permitted monitoring of the SAM coverage formation over time. The time constants derived from fitting the time-dependent current to the rearrange-limited Langmuir model agreed well with previously reported results determined using other techniques, demonstrating that our simple method can reliably characterize SAM adsorption kinetics.

Keywords: Self-Assembled Monolayer, Microelectrode, Steady-State Current, Blocked Electrode, Adsorption Kinetics

1. INTRODUCTION

Self-assembled monolayers (SAMs) covalently immobilized on gold surfaces *via* a thiol–Au bond have attracted considerable interest. They are used in a variety of applications, particularly in nanotechnology, to tailor the physical and chemical properties of a surface [1]. SAM-formation protocols often involve immersing a clean substrate in a dilute ethanolic solution overnight. However, the SAM adsorption kinetics depend on several factors, such as the adsorbate concentration and temperature [1,2]. The chemical structure of the adsorbate can strongly influence the self-assembly mechanism. The synthetic accessibility of organic adsorbates enables easy anchoring of a variety of complex molecules, and the number of compounds that may be used to form SAMs has multiplied. Although the formation of SAMs using *n*-alkanethiol systems appears straightforward, other chemical structures can affect both the kinetics and structure of a SAM as the slower adsorption kinetics of biphenyl thiols was reported previously owing to the stiffness, the conjugation between the substituent and the thiol group, and the molecular dipole [3].

Therefore, it is essential to understand the formation process of SAM on individual compounds. Several *in situ* or *ex situ* techniques have been used to monitor SAM formation, including ellipsometry [4], scanning tunneling microscopy (STM) [5], atomic force microscopy (AFM) [6], quartz crystal microbalance measurements [7,8], second harmonic generation (SHG) [9], surface plasmon resonance (SPR) [10-12], and electrochemistry [13,14]. However, the adsorption kinetics of many adsorbates remain largely uncharacterized, especially during solution-phase assembly, because such techniques are time-consuming, provide limited temporal resolution, and require expensive equipment. There is a need for a simple low-cost experimental technique that permits measuring adsorption kinetics in solution phases. Electrochemistry provides a sensitive, easy, and affordable method for investigating the growth of SAMs *in situ* and in real time.

SAM modifications can block electrodes in cyclic voltammetry (CV) measurements, and this property has been widely used to confirm the well-ordered packing of SAMs on a surface [15]. The extent of surface passivation toward electron transfer in the context of electrochemistry provides a simple and valuable means for probing the integrity of SAMs, which optimally form an barrier that is impermeable to redox species in the electrolyte solution.

Passivation measurements as a function of time are suitable for *in situ* characterization of self-assembly processes. For example, SAM coverage may be calculated from measurements of the degree of faradic current blocking as a function of time at a constant potential, as is measured in chronoamperometry. *In situ* measurements of the faradic current in chronoamperometry are complicated because even on clean electrodes the faradic current declines over time due to the thickening diffusion layer, as described by the Cottrell equation [16]. Time-independent chronoamperometry current measurements permit a simpler analysis of the coverage by measuring variations in the faradic current without the need to consider the electrolysis time. The problem of the current decline over time can be circumvented by enhancing mass transport to generate a steady-state current.

Recently, our group reported the *in-situ* real-time electrochemical measurement of kinetics of thiol adsorption using rotating disk electrode [17], in which variations in the steady-state current are then directly related to the degree of blocking or coverage by adsorbates. Instead of RDE, the microelectrode also enhances the mass transfer analogous to the operational mechanism of scanning electrochemical microscopes (SECMs), which detect distances by measuring deviations in a steady-state faradic current [18].

Herein, we report a simple and affordable method for *in situ* real-time monitoring of thiol self-assembly using an electrochemical steady-state current with microelectrode. The steady-state faradic current decreases caused by surface passivation by forming a SAM, which determine the coverage by simple measurements of the current over time without the use of a special apparatus.

2. EXPERIMENTAL PART

2.1. Chemicals

11-Mercaptoundecanoic acid and all other chemicals (obtained from Aldrich or Sigma) were of analytical or better grade and were used as received. All glassware and electrochemical cells were cleaned with Nochromix (Godax Lab., Inc.) cleaning solution and rinsed with ultrapure water and ethanol.

2.2. Electrochemical measurements

Electrochemical experiments were performed using a CHI potentiostat 660D (CH instruments, Austin, TX). The three-electrode electrochemical cell consisted of the Au working electrode, a Pt wire counter electrode and an Ag/AgCl (3 M NaCl) reference electrode (Bioanalytical Systems, West Lafayette, IN). Microelectrode measurements were obtained using gold working electrode (12.5 μm diameter, CHI105, CH instruments, Austin, TX). All working electrodes were polished with alumina and cleaned in water and ethanol in an ultrasonic bath. Then, electrodes were cleaned for 3 min in piranha solution (3:7 by volume 30% H_2O_2:H_2SO_4, *Caution: piranha solution reacts violently with most organic materials and must be handled with extreme care*), rinsed with H_2O and ethanol, and dried under a stream of nitrogen.

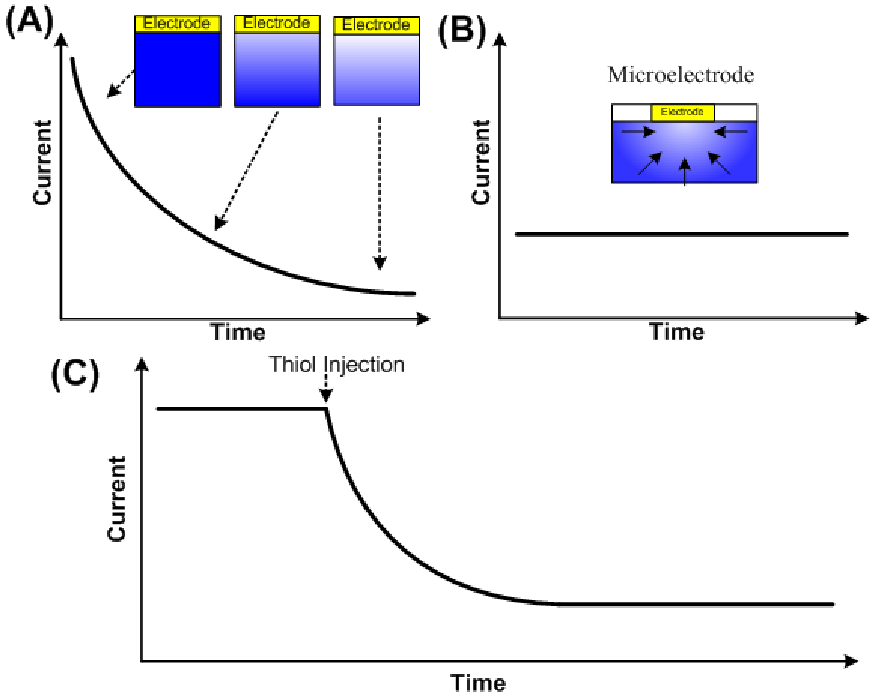
2.3. Estimation of the Adsorption Kinetics

Data of the normalized current ratio were converted to the coverage from which the values of the rearrange-limited Langmuir model were calculated. In order to fit the lines, we used the open-source software Peak-O-Mat, which runs on SciPy (Scientific Python). Peak-O-Mat is an interactive program that is designed to fit curves using a least-squares algorithm to a user-specified function. Equation 6 in the manuscript for the rearrange-limited Langmuir model was used for the fitting.

3. RESULTS AND DISCUSSIONS

Scheme 1 depicts the principles of in-situ real time electrochemical measurements of kinetics of thiol adsorption using microelectrode. By applying a sufficiently positive potential, a redox active molecule of ferrocene in the ethanolic solution is oxidized to generate a faradic current. While the current on the stationary macroelectrode declines over time due to semi-infinite linear diffusion, as shown in Scheme 1(a), mass transport enhanced by a microelectrode stabilize the faradic current to a steady-state value, as shown in Scheme 1(b). A steady-state current is observed in the absence of adsorbates or a SAM on the electrode surface, and injection of thiol-containing molecules to form a passivating SAM on the electrode decreases the faradic current, as shown in Scheme 1(c). Deviations from the steady-state current are proportional to the degree of blocking, i.e., the surface packing of the

SAM. Therefore, self-assembly of the thiolate on gold can be monitored simply by measuring the current *in situ* in an ethanolic solution in real time.



Scheme 1. Current–time response (a) at a stationary macroelectrode on which current decayed due to thickening of the diffusion layer, (b) at microelectrode, which generated the steady-state current by radial diffusion, and (c) at microelectrode, showing the decrease in steady-state faradic current due to oxidation of ferrocene upon formation of the insulating SAM.

Figure 1 shows the chronoamperometric responses measured in 9 mL of an ethanol solution containing 1 mM ferrocene (FC) and 0.1 M $LiClO_4$ in the presence of a gold microelectrode (12.5 μm diameter) at a potential of 0.6 V *vs.* Ag/AgCl. The electrode response was normalized with respect to the current for the oxidation of ferrocene at time t = 0, at which point the thiolate solution was injected into the cell. In the absence of thiol molecules, the current ratio was nearly constant, approaching steady-state conditions. The oxidation of ferrocene proceeded at a constant rate because mass transport was enhanced by the radial diffusion, thereby establishing a stable baseline, as shown in the red line of Figure 1. To monitor the self-assembly process, 1 mL of an ethanol solution containing 10 mM 11-mercaptoundecanoic acid (MUA), 1 mM ferrocene, and 0.1 M $LiClO_4$ was injected into the electrochemical cell, and the faradic current was recorded continuously. Figure 1 shows the chronoamperometric response during the self-assembly of a MUA SAM. The steady-state current produced by the oxidation of ferrocene gradually decreased over time due to surface passivation by formation of a SAM. A rapid decrease in the current ratio during the early stages indicated the fast adsorption of the thiol head group to the gold surface. Annealing of the adsorbate followed, as indicated by the slowing of the current ratio decrease. Finally, the current blocked by SAM exhibited the constant value after ca. 4 hours. (inset in Figure 1) These two regimes agreed with a recent report, which described the process for thiolate self-assembly as a two-step process [2,4,5,9-14]. Because microelectrodes do not require additional special equipment, such as electrode rotators, and because they can be combined with standard commercially available electrochemical instruments, microelectrodes allow more readily accessible configurations for the *in situ* monitoring of SAM generation. These features demonstrated that self-assembly of thiolates on gold may be monitored by measuring the deviations from a steady-state faradic current on a microelectrode.

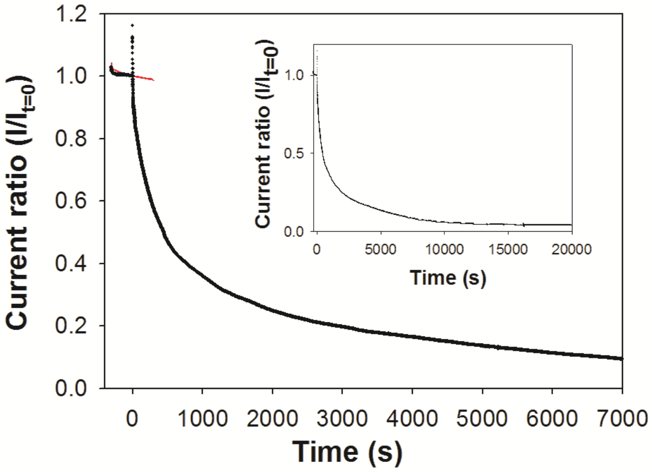
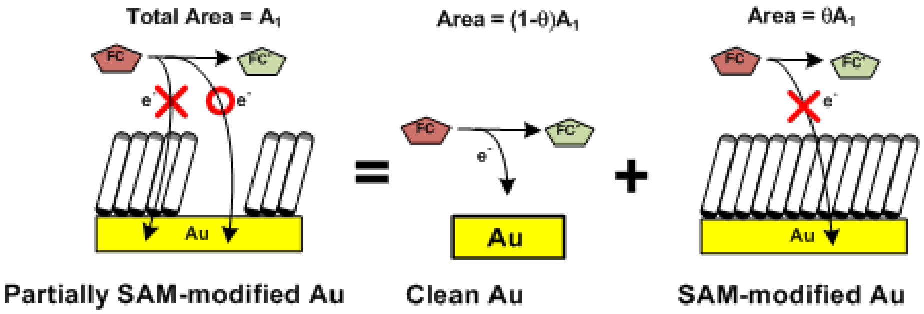


Figure 1. Normalized current–time responses at 0.6 V *vs.* Ag/AgCl in the ethanolic solution containing 1 mM ferrocene and 0.1 M $LiClO_4$ on Au disk microelectrode. The thiol solution containing 10 mM 11-mercaptoundecanoic acid, 1 mM ferrocene, and 0.1 M $LiClO_4$ was injected at time t=0 and the red line indicates the control experiments without MUA injection. Normalized current-time response measured during 20000 s (inset).



Scheme 2. Schematic diagram of a gold surface during self-assembly. The heterogeneous surface included two regions containing either clean gold (a SAM-uncovered region) or a SAM-modified surface. SAM coverage (θ) at each time determined the areas covered by the two region types.

The relationship between the recorded current and the MUA SAM surface coverage (θ) enabled estimation of the kinetics of formation of the SAM. The steady-state current for a disk microelectrode under mass transport-limited conditions is given by the expression [19,20]

$$i_{ss} = \frac{4nFDC^*}{\pi r} A = 4nFDC^* r\,, \qquad (1)$$

where i_{ss} is the steady-state current in which the mass transfer of FC is sufficiently fast that the concentration at the electrode surface is equal to the bulk concentration. F is the Faraday constant, n is the viscosity of the solution, D is the diffusion coefficient, C* is the concentration of FC, and r is the radius of the disk electrode. The gold surface during the self assembly of MUA can be considered as heterogeneous surface composed of two different regions shown in Scheme 2. One is a clean gold area and the other is a MUA-modified SAM. Thus, the observed faradic current is the sum of these two current. During self-assembly, the gold electrode surface includes regions of clean gold, described by eq (1), and regions of the MUA SAM, described by eq (2). In contrast, the electron-transfer rate constant by tunneling through SAM decrease exponentially with the length of MUA making the electron-transfer irreversible, i. e. kinetically controlled condition. Then, the very slow electron transfer kinetics on the MUA SAM is given by

$$i_k = nFk_f(E)C^* A = nFk_f(E)C^* \pi r^2\,. \qquad (2)$$

The observed current is described as the sum of the two currents,

$$i = i_{Au} + i_{SAM} \approx i_{ss,Au} + i_{k,SAM} = \frac{4nFDC^*}{\pi r}\pi r^2(1-\theta) + nFk_f(E)C^*\pi r^2\theta\,. \qquad (3)$$

Where θ is the normalized monolayer coverage. The current prior to introduction of the MUA is given by

$$i_{t=0} = 4nFDC^* r\,. \qquad (4)$$

Dividing eq (3) by eq (4) gives the current ratio,

$$I = \frac{i}{i_{t=0}} = (1-\theta) + \frac{\pi k_f(E)}{4D} r\theta = 1 - s\theta\,, \qquad (5)$$

where $s = 1 - \frac{\pi k_f(E) r}{4D}$. Eq (4) and eq (9) indicate that the normalized current ratio (I) is linearly related to the MUA coverage (θ). To evaluate the value of s in equation 4, the current on the fully covered MUA SAM was measured. The current at 1 mM MUA did not change significantly as shown inset in Figure 1. The current at 20000 s, therefore, corresponded to the fully covered MUA SAM, and the current was converted to the coverage (s=0.9591)., and s is the proportionality constant.

The plots of the surface coverage over time were fit to previously proposed models. Among the models presented thus far, the rearrange-limited Langmuir model [10,12,21] described the experiments best, as shown in Figure 2, over the entire experimental period. Briefly, this model assumes fast adsorption of the thiol head groups at the gold surface during the first step, followed by slower surface crystallization processes in which the alkyl chains get out of the disordered state and form a two-dimensional crystal. This process is described by

$$\theta = F_1(1-e^{-k_1 t}) + F_2(1-e^{-k_2 t}), \qquad (6)$$

where F_1 and F_2 are the limiting coverage increases at each step, k_1 and k_2 are the rate constants for fast adsorption in the first step and slow rearrangement in the second step, respectively.

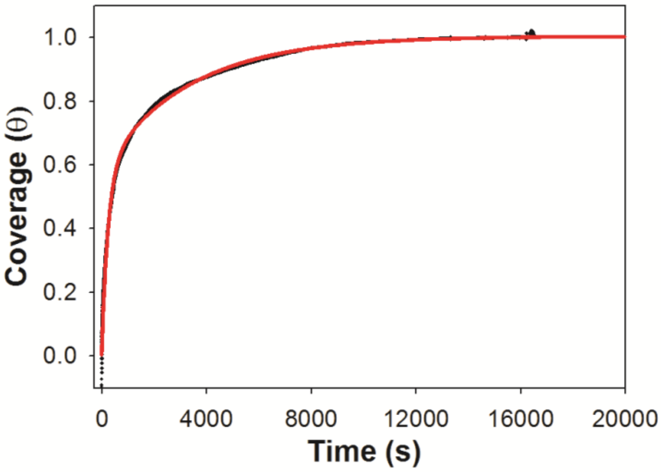


Figure 2. Adsorption of 1 mM 11-mercaptoundecanoic acid in ethanol containing 1 mM ferrocene and 0.1 M $LiClO_4$ onto the microelectrode (black line). The red line indicates the curve calculated from the rearrange-limited Langmuir model.

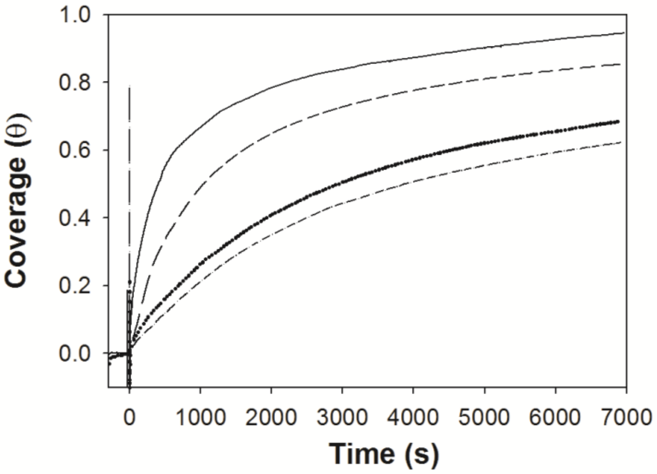


Figure 3. Adsorption of different concentrations of MUA onto the microelectrode in ethanol containing 1 mM ferrocene and 0.1 M $LiClO_4$. (a) 1 mM (solid line), (b) 500 µM (dashed line), (c) 100 µM (dotted line), (d) 50 µM (dash-dot line).

This model was applied to the MUA adsorption kinetics for concentrations ranging from 50 μM to 1 mM. Figure 3 shows plots of the coverage *vs.* time for adsorption at different concentrations of MUA. Two distinct time constants were discerned, and the rate of adsorption increased with MUA concentration. The fits to various concentrations are presented in Table 1. The increase in the rate of adsorption during the first step with increasing concentration of MUA was evident, although the relationship between k_1 and concentration was complicated [12]. Although the order of magnitudes agreed, the estimated values of k_1 and k_2 in the MUA ethanolic solution in the cell with microelectrode were slightly lower than the values previously measured for this system using SPR or RDE with the rearrange-limited Langmuir model [12,17]. Rough surface of microelectrode [22] might be the origin of the relatively slow kinetics decreasing the organization speed and following adsorption. In addition, the contribution of edge effect of microelectrode cannot be excluded. It is worth noting that the magnitude of the applied potential can affect the adsorption kinetics of thiol molecules [23] and/or the organizational process though potential-assisted organization is often not observed depending on the applied potentials [24]. Nonetheless, such a potential-dependent process is not obvious in our experimental condition. This analysis confirmed that electrochemical steady-state current can provide an appropriate method for monitoring the formation of SAMs, and the rate constants derived from this method agree with those derived from SPR experiments.

Table 1. Fitted k_1 and k_2 values Determined from Raw Data based on Rearranged-Limited Model as a Function of MUA concentration

MUA (μM)	**k_1**			**k_2**		
	μ-electrode	RDE[a]	SPR[b]	μ-electrode	RDE[a]	SPR[b]
1000	0.0068	0.011	0.012	0.0004	0.0009	0.0004
500	0.0022	0.0086	0.006	0.0004	0.0006	0.0003
100	0.0019	0.0037	0.0024	0.0003	0.0003	0.00010
50	0.0012	0.0011		0.0003	0.0003	

[a] From Ref. 17

[b] From Ref. 11

4. CONCLUSIONS

In conclusion, steady-state faradic current measurements provide a simple affordable method for monitoring the adsorption kinetics of 11-mercaptoundecanoic acid on a gold surface *in situ* in real time in the solution phase. Surface passivation by forming a SAM decreases the faradic current so that the coverage may be determined by simple measurements of the current over time without the use of a special apparatus. The obtained results agreed well with previous results obtained using other techniques, demonstrating that our method provides a reliable alternative technique for characterizing adsorption kinetics. This method is easy to use, inexpensive, and permits characterizing the self-assembly kinetics of newly synthesized molecules.

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