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Selective Anodic Desorption for Assembly of Different Thiol Monolayers on the Individual Electrodes of an Array

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Abstract

The close proximity of two individually addressable electrodes in an interdigitated array provides a unique platform for electrochemical study of multi-catalytic processes. Here we report a “plug-and-play” approach to control the underlying self-assembled monolayer and the electroactive species on each individually addressable electrode of an interdigitated array. The method presented here uses selective anodic desorption of a monolayer from one of the individually addressable electrodes and rapid formation of a different self-assembled monolayer on the freshly cleaned electrode. We illustrate this strategy by introducing variations in the length of the linker to the electroactive species in the self-assembled monolayer, which determines the rate of electron transfer. In order to separate the assembly of the monolayer from the choice of the electroactive species we use Cu^I-catalyzed triazole formation (“click” chemistry) to covalently attach an acetylene-terminated electroactive species to an azide-terminated thiol monolayer selectively on each electrode. The resulting variations in the electron-transfer rate to surface-attached ferrocene and in the rate of catalytic oxidation of ascorbate by the ferrocenium/ferrocene couple demonstrate an application of this approach.

Keywords

Interdigitated array; SAM; click; Electron transfer; IDA; self-assembled; monolayer

Introduction

In this study we demonstrate independent control over the self-assembled monolayer and the appended functionality on each electrode of an interdigitated array of microelectrodes (Figure 1). This control will provide us a useful platform for future study of multi-electron, multi-catalytic processes involving the generation or consumption of highly reactive species. For instance, interdigitated microelectrodes provide a greater sensitivity for the detection of short-lived side products than can be achieved by the rotating ring-disk method.¹ This sensitivity is achieved by the close proximity of two parallel electrodes (1–10 μm separation). We will use self-assembled monolayers to control the surface composition and structure of catalysts on each electrode. Self-assembled monolayers have proven to be a flexible way to functionalize electrode surfaces for a variety of applications.^{2,3} We have previously shown the versatility of the triazole-forming “click” reaction between an azide-terminated self-assembled monolayer on a gold electrode and an appended acetylene on an electroactive species.⁴ This mild reaction is specific, high yielding, and forms a stable triazole linker⁵ that does not significantly inhibit electron transfer.⁶ Recently, we reported a method for covalently attaching

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different species to the self-assembled monolayer on each of the independent electrodes of an interdigitated array by electrochemical activation or deactivation of the Cu(I) coupling catalyst used for the “click” reaction.⁷ Here, we report a method that adds further versatility by providing independent control of the monolayer on each of the electrodes.

The challenge in selective formation of different self-assembled monolayers on each electrode is in the deposition of the second monolayer. Our solution to this challenge uses selective anodic desorption of an initial thiol monolayer from one electrode and the rapid formation of a different well packed thiol monolayer onto that electrode. Fast monolayer deposition is required to minimize exchange of solution-phase thiols with the thiols adsorbed in the existing monolayer on the adjacent electrode. Deposition of a dense self-assembled monolayer within 1 minute was achieved after anodic desorption of the original monolayer.

Results and discussion

We first describe the anodic desorption and thiol-monolayer deposition procedures. A gold electrode that had not yet had a monolayer deliberately adsorbed to its surface was cleaned by holding its electrochemical potential at +1.65 V vs Ag/AgCl/NaCl in 0.5 M aqueous H₂SO₄ for 15 s. We consider a stable gold-reduction peak at +0.860 V in sequential cyclic voltammograms from 0 V to +1.65 V and back to 0 V to be an indication of a clean electrode surface (Figure S1 supporting information). The electrode was then rinsed with water and ethanol and exposed to a solution of 0.4 mM HS(CH₂)₁₅CH₃ in ethanol for 1 minute. The specific capacitance (2 $\mu\text{F}\cdot\text{cm}^{-2}$) and blocking of K₃Fe(CN)₆ reduction at this electrode were consistent with previous reports for formation of a well packed monolayer⁸ (Figure S2 supporting information). The self-assembled monolayer was desorbed by holding the electrode potential at +1.8 V for 30 s and then cycling the potential from 0 V to +1.65 V and back to 0 V until the gold cyclic voltammogram showed a stable reduction peak at +0.860 V vs Ag/AgCl/NaCl.

Using this procedure to clean an electrode and rapidly form a self-assembled monolayer, we developed a stepwise approach to control the monolayer on each electrode of an interdigitated array (Figure 2). This requires deposition of different azide and diluent thiols on each individually addressable electrode. The interdigitated electrodes were anodically cleaned⁹ and then immersed in a solution that contained 0.1 mM HS(CH₂)₁₆N₃ and 0.3 mM HS(CH₂)₁₅CH₃¹⁰ in ethanol for 1 minute. The mixed azide-terminated monolayers were incubated for 3 hrs in a 10 mM CH₃(CH₂)₁₅SH solution in ethanol to displace weakly adsorbed azide-terminated thiols. Anodic desorption of the thiols from electrode **1** was then carried out (vide supra). An acetylene-terminated electroactive molecule (ethynyl ferrocene) was attached using “click” chemistry.¹¹ This resulted in an electroactive catalyst covalently bonded to the desired monolayer on electrode **2** while electrode **1** remained bare.¹² The array was then immersed in a solution that contained 0.1 mM HS(CH₂)₁₁N₃ and 0.3 mM HS(CH₂)₇CH₃ in ethanol for 1 minute to form a different monolayer on electrode **1**. Subsequent attachment of ethynyl ferrocene to electrode **1** results in the same electroactive molecule being attached to a different self-assembled monolayer on each electrode.

Variation of the length of the azide-terminated and diluent thiols influences the rate of electron transfer.¹³ Figure 3 shows the voltammograms of electrode **1** and electrode **2**. The slow rate of electron transfer to the appended ferrocene on electrode **2** is evidenced by a large peak-to-peak separation ($k_{\text{et}} = 2.0 \text{ s}^{-1}$).⁶ The shorter monolayer on electrode **1** allows for a reversible ferrocene redox wave at the scan rate used, indicating a faster rate of electron transfer.

Wang and coworkers¹⁴ have reported another method to selectively adsorb different monolayers on the two electrodes of an array. They reported the electrochemically induced

formation of a self-assembled monolayer on one gold electrode held at -1.5 V vs. Ag/AgCl for 1 minute in the presence of another electrode at open circuit. The authors suggested that both electrodes in their system might be initially protected by some adventitious adsorbate and that the negative potential enabled its cathodic desorption and rapid replacement by the desired thiol. In our system, after anodically cleaning both electrodes in 0.5 M H₂SO₄, applying -1.5 V vs Ag/AgCl/NaCl¹⁵ to electrode **1** while electrode **2** was at open circuit, resulted in the formation of monolayers with similar coverage on both electrodes (Figure S4 supporting information). This result supports Wang and coworkers' hypothesis that the electrochemically induced formation of a thiol monolayer in their system was due to cathodic desorption of a pre-existing adsorbate.¹⁴ In a brief survey of possible blocking adsorbates, we did not find conditions under which a desired thiol monolayer could be formed at the electrode held at the negative potential while the electrode at open circuit remained free of the thiol; whenever a monolayer was formed at the negative electrode, significant thiol adsorption also occurred at the other electrode. However, we did not make an exhaustive study of the options, and Wang's cathodic method is likely to be preferable to our anodic method in certain circumstances.

We next wanted to check that different catalysts could be selectively deposited on each of the electrodes of our system.¹⁶ Both electrodes of an interdigitated array were anodically cleaned and a mixed thiol monolayer was formed on both electrodes using a solution containing 0.1 mM HS(CH₂)₁₁N₃ and 0.4 mM HS(CH₂)₇CH₃ in ethanol for 1 minute, followed by immersion in a 10 mM solution of CH₃(CH₂)₇SH for 3 hr to remove weakly adsorbed azide-terminated thiols. Selective anodic desorption of the thiol monolayer from electrode **1** was accomplished by anodic cleaning in 0.5 M H₂SO₄ until a stable gold cyclic voltammogram was obtained, while keeping electrode **2** at open circuit. The ethynyl ferrocene moiety was then clicked onto the azide-terminated monolayer using standard procedures. Deposition from the same mixed thiol solution (0.1 mM HS(CH₂)₁₁N₃ and 0.4 mM HS(CH₂)₇CH₃ in ethanol) was followed by "click" reaction with propynone ferrocene. This resulted in an interdigitated array having two different electroactive species, with nominally identical monolayers on each individually addressable electrode. This is evident by the simultaneous cyclic voltammograms of electrode **1** and electrode **2**. The two electrodes show redox features that are 180 mV apart with very little cross contamination (Figure 4).

The procedure described above for obtaining different monolayers on each electrode relies on rapid formation of the new monolayer on the anodically cleaned electrode before significant exchange can occur between the thiols in solution and those in the original monolayer on the other electrode. Various procedures and suggested times have been reported for the formation of thiol monolayers on gold:¹⁷ these include overnight deposition,¹⁸ oxidative deposition (15 minutes at 600 mV),¹⁹ and reductive deposition (1 minute, -1.5 V)¹⁴ in an ethanolic solution of thiols. To explore the degree of cross-contamination during formation of the second monolayer, a single electrode coated with the ferrocene-modified monolayer was exposed to the same mixed thiol solution for different periods of time and then treated with the "click" solution containing propynone ferrocene. After 1 minute of exposure to the thiol solution followed by the click solution for the standard period of time, the cyclic voltammogram showed no indication of the exchange of the existing thiols in the monolayer by fresh azide-terminated thiols (Figure 5). After exposure for 15 minutes, the presence of the redox peak from propynone ferrocene indicates that some exchange has occurred.

Our strategy allows the study of the effect of the rate of electron transfer on the overall rate of catalytic reactions at different electrodes in an array. Figure 6 shows, as an example, the oxidation of ascorbate catalyzed by the ferrocenium/ferrocene couple. For the monolayer that allows fast electron transfer, a much higher catalytic current is observed, even though the coverage of ferrocene on the slower monolayer is higher. This result indicates that the kinetics of the reaction between ferrocenium and ascorbate is sluggish relative to the rate of electron

transfer in the monolayer with fast electron transfer but slow relative to the rate of electron transfer at the slow monolayer. This example demonstrates the versatility of our preparative method for studying catalytic reactions.

In conclusion, we have demonstrated selective control over two parameters on each of the individually addressable electrodes of an interdigitated array: the electroactive catalyst and the underlying self-assembled monolayer. We have described a stepwise approach using selective anodic desorption of the thiol monolayer from one of the electrodes of an interdigitated array and the rapid deposition of another thiol monolayer. We have demonstrated that this approach allows independent; Cu^I-catalyzed “click” reactions of different acetylene-terminated electroactive species on each of the individually addressable microelectrodes. Control over the monolayer adsorbed on either electrode was illustrated by the electron-transfer rate to the electroactive species on each of these microelectrodes. The coverage of the catalyst can be controlled by variations in the fraction of the azide-terminated thiols in the mixed thiol solution. In addition to these parameters, the interdigitated microelectrode spacing can be changed as needed which makes this a versatile tool for studying complex electrochemical systems.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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9. Prior to the formation of a thiol monolayer, the electrodes were anodically cleaned in 0.5 M H₂SO₄ solution by cycling from 0 - +1.65 - 0 V until a stable reductive wave was obtained, rinsed with water, and ethanol, and used immediately. Similar anodic cleaning results were obtained in 0.5 M HClO₄ and in a pH 7 phosphate buffer containing 0.1 M KPF₆.
10. The initial deposition of the longer thiols is advantageous because they form more stable monolayers on Au, and therefore are less perturbed by the anodic desorption of the thiols on the adjacent electrode. This strategy also minimizes the possibility of exchange with the second thiol solution.
11. It is preferred that the anodic desorption procedure be performed prior to the attachment of the electroactive species onto the electrode. It was observed that anodic desorption of thiols from electrode 1 leads to decay of ferrocene when it is attached to electrode 2 prior to the desorption step (Figure S3 supporting information). This loss of coverage was also observed when the desorption was carried out in 0.1 M HClO₄, or pH 7 buffer containing 0.1 M KPF₆. However this process is less damaging if electrode 1 contains azide functionality.
12. A single (250 mVs⁻¹), cyclic voltammogram (0-1.65-0 V) in 0.5 M aqueous H₂SO₄ or pH 7 phosphate buffer containing 0.1 M KPF₆ is recommended after the click reaction to ensure a clean surface for deposition of the second monolayer.

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15. For our studies, mixed thiol solutions with a 0.4 mM total concentration in ethanol containing 2 mM LiClO₄ was used for the reductive deposition. This low concentration of electrolyte results in the formation of a monolayer with a lower charging current than was obtained with higher LiClO₄ concentrations.
16. The method described here uses a chemical reductant to form the CuI catalyst for the “click” reaction. This approach is complementary to the electrochemical activation and deactivation of the coupling catalyst for a selective “click” reaction on a given electrode (ref 7).
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Figure 1.

Plug-and-play approach to study complex electrocatalytic processes using interdigitated microelectrodes. Three parameters may be varied: (i) the catalytic species attached to each electrode, (ii) the linker and the diluent in the underlying self-assembled monolayer on each electrode, and (iii) the electrode geometry and spacing. The numbering of the catalysts, linkers, diluents and electrodes corresponds to the order of procedures in this report.

Figure 2.

Procedure to deposit different self-assembled monolayers modified with electroactive species on each electrode of an Au/Au interdigitated array.

Figure 3.
Cyclic voltammograms at $5000 \text{ mV} \cdot \text{s}^{-1}$ of each of the electrodes prepared as described in Figure 2.

Figure 4. Simultaneous cyclic voltammograms of electrode 1 and electrode 2 in 0.1 M HClO_4 ($5000 \text{ mV} \cdot \text{s}^{-1}$), showing two different electroactive molecules on each of the independently addressable electrodes of the interdigitated array. Ferrocene (Fc) on electrode 2, propynone ferrocene (FcCO) on electrode 1.

Figure 5.

The effect of exposure of a ferrocene-terminated mixed monolayer to a $\text{HS}(\text{CH}_2)_{10}\text{N}_3/\text{HS}(\text{CH}_2)_7\text{CH}_3$ solution in ethanol followed by clicking with propynone ferrocene. Initial cyclic voltammogram (solid line —), after 1 minute in the thiol solution (dot-dot-dashed line ···), and after 15 minutes (dashed line ---) (scan rate $1000 \text{ mV}\cdot\text{s}^{-1}$ in 1M HClO_4).

Figure 6.

(a) Cyclic voltammogram ($5000 \text{ mV}\cdot\text{s}^{-1}$) of electrode **1** (prepared from 0.1 mM HS $(\text{CH}_2)_{10}\text{N}_3$ and 0.3 mM HS $(\text{CH}_2)_7\text{CH}_3$) and electrode **2** (prepared from 0.15 mM HS $(\text{CH}_2)_{18}\text{N}_3$ and 0.25 mM HS $(\text{CH}_2)_{15}\text{CH}_3$) in pH 7 buffer with 0.1 M KPF_6 showing ferrocene molecules attached to a different self-assembled monolayer on each of the independently addressable electrodes of the interdigitated array. (b) Shows the catalytic oxidation of 0.01 M ascorbic acid with ferrocene attached to the surface in pH 7 buffer ($100 \text{ mV}\cdot\text{s}^{-1}$), demonstrating the effect of the electron-transfer rate from ferrocene on the catalytic oxidation of ascorbate.