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Synthesis and Characterization of Simple Self-Assembling, Nanoporous
Monolayer Assemblies: A New Strategy for Molecular Recognition

by

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**Synthesis and Characterization of Simple Self-Assembling,
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Molecular Recognition.**

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30 June, 1992

ABSTRACT

Composite monolayer films spontaneously adsorb onto the surface of Au from an ethanolic mixture of two mercaptans to form a nanoporous surface. The monolayers consist of an electron transfer-retarding *n*-alkanethiol framework, which passivates the Au surface, and a much shorter aromatic mercaptan which induces molecule-sized defects within the passivating framework.

Electrochemical experiments indicate that the chemical nature of the template and the template/framework ratio of the deposition solution control the size, number, and chemical characteristics of the defects. For example, 4-hydroxythiophenol/1-hexadecanethiol mixed monolayers yield monolayer assemblies that admit $\text{Ru}(\text{NH}_3)_6^{3+}$ probe molecules but not $\text{Fe}(\text{CN})_6^{3-}$.

INTRODUCTION

We wish to report the synthesis and characterization of two-component, self-assembling monolayers that act as nanoporous molecular recognition membranes. The framework component prevents probe-molecule penetration through the monolayer membrane, and the template component induces defect sites within the inert framework which permit probe-molecule penetration. The degree of penetration is controlled by the chemical and physical characteristics of the probe and template molecules. The number of the defect sites can be reproducibly varied by changing the relative concentrations of the template and framework molecules in the solution from which the monolayer assembles.

Self-organizing chemical systems represent a versatile approach for the rational modification of surfaces.¹ During the past several years, significant effort has been directed towards the synthesis and characterization of ideal, defect-free mono- and multilayers.²⁻⁷ However, little emphasis has been placed on synthesis and analysis of intentionally-formed defect structures.⁸⁻¹⁰

Sagiv was the first to report the intentional perforation of self-assembling, surface-confined monolayers of alkylsiloxanes, and he showed that such membranes could effectively readsorb molecules of approximately the same size and shape as the molecules used to induce the perforations.⁸ Kim et al. applied surface enhanced Raman spectroscopy to the analysis of related monolayer structures and confirmed Sagiv's results.⁹ More recently, Bilewicz and

Majda¹⁰ have shown that Langmuir-Blodgett (L-B) films containing molecules that disrupt the passivating nature of the L-B monolayer can be transferred intact to electrode surfaces. The electrodes thus modified display electrochemical responses which range from that of an unpassivated surface to that of a totally passivated surface depending on the number of "gate" sites originally spread onto the L-B subphase.

Our approach to synthesizing and characterizing molecular recognition sites is illustrated in Scheme I. First, a clean Au

Scheme I

substrate is exposed to a dilute mixture of two mercaptans. The *n*-alkanethiol molecules act as an inert electron- and mass-transfer blocking layer,^{1-6,11-13} while the functionalized, aromatic organomercaptan molecules act as electron-transfer sites. The number of defect sites on the surface is a function of the relative concentrations of the two mercaptans in the bulk deposition solution.¹⁴ In this paper, we demonstrate that the size, number, and chemical characteristics of defect sites can be reproducibly controlled, and we analyze the electrochemical response of the perforated monolayers in terms of a theory developed by Amatore et al.,¹⁵ which is qualitatively summarized by the cyclic voltammetry responses shown on the right side of Scheme I.

EXPERIMENTAL SECTION

1-Hexadecanethiol ($C_{16}SH$), $HS(CH_2)_{15}CH_3$, (Aldrich, 99%) was purified by double distillation. 4-hydroxythiophenol (4-HTP), $HS(C_6H_4)OH$, (Aldrich, 90%); 4-thiocresol (4-TC), $HS(C_6H_4)CH_3$, (Aldrich, 98%); hexammineruthenium (III) chloride, $Ru(NH_3)_6Cl_3$, (Strem); and potassium ferricyanide, $K_3Fe(CN)_6$, (Aldrich) were used without further purification; however, we verified that purification of 4-HTP by sublimation did not significantly change the electrochemical results. Water was purified by a Milli-Q System (Millipore).

Electrochemical experiments were carried out in a single-compartment, three-electrode, glass cell containing a Ag/AgCl, KCl (sat'd) reference electrode and a Pt counter electrode. Working electrodes were prepared as follows: Au flag electrodes (1 x 2 cm) were cut from 0.1 mm-thick Au foils (Aesar, 99.95%). The Au flags were electrochemically cleaned,¹⁶ polished,¹⁷ and annealed in a calibrated Lindberg Model 55035 tube furnace at 1055 C for 5 h in flowing Ar (170 mL/min). The cleaning process was then repeated. Just prior to surface modification, the Au electrodes were cleaned by dipping in freshly prepared "piranha solution" (3:1 conc. H_2SO_4 :30% H_2O_2) for 5 min and then in 6 M HCl for 10 s. (Caution: piranha solution reacts violently with organic compounds, and it should not be stored in closed containers.) Surface modification was carried out by soaking each electrode in an ethanol solution containing two mercaptan derivatives for at least 36 h.

All electrochemical experiments were performed with a Pine Instruments Model AFRDE4 bipotentiostat, and data were recorded on a Kipp and Zonen Model BD-90 X-Y recorder.

RESULTS AND DISCUSSION

The cyclic voltammetry results shown in Figure 1 were

Figure 1

obtained from an electrode prepared by soaking Au foils in ethanol solutions containing various ratios of 4-HTP, the defect-inducing organomercaptan $\text{HS}(\text{C}_6\text{H}_4)\text{OH}$, and C_{16}SH , the framework *n*-alkanethiol $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$. Following modification, the electrode potential was cycled between +0.3 and -0.5 V at 0.1 V/s in an aqueous electrolyte solution consisting of 5 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ and 1.0 M KCl. In the presence of defect sites that have the correct combination of size and intermolecular interaction energies, the $\text{Ru}(\text{NH}_3)_6^{3+}$ probe molecules should penetrate the inert framework and undergo electron exchange with the underlying Au surface. The electron transfer should be facile, since the electron transfer rate constant for $\text{Ru}(\text{NH}_3)_6^{3+}$ is large.^{10a,18} If the probe molecules can not penetrate the monolayer framework, they can only be reduced by electrons that tunnel through the C_{16}SH layer. Since the distance of closest approach of the probe to the electrode surface is approximately the thickness of the monolayer, about 21 Å,⁴ the

tunneling current should be small relative to that arising from direct electron transfer at defect sites.

Figure 1a shows the result obtained for a nominally defect-free $C_{16}SH$ monolayer surface. The roughly exponential shape of the cyclic voltammogram and the magnitude of the maximum cathodic current are consistent with electron tunneling through the film.^{3b,5,10,11}

Figure 1b shows the behavior of an electrode modified in a solution containing 4-HTP and $C_{16}SH$ in a 1/1 ratio. Several important observations concerning these data follow: First, the maximum cathodic current is about five times higher than that of the completely passivated electrode, Figure 1a. Since these data are easily reproduced, we ascribe the current increase to surface defects induced by the template; the defects permit $Ru(NH_3)_6^{3+}$ to penetrate the monolayer framework. Second, the shape of the cyclic voltammogram is approximately sigmoidal, rather than exponential, and similar to that expected for an array of microelectrodes.^{10,15,19} This suggests that the template-induced defects are small and widely spaced relative to the diffusion layer thickness, since either large defects or closely-spaced small defects will result in peak-shaped cyclic voltammograms that are characteristic of linear diffusion.^{10,15,19,20} Third, since the concentrations of template and framework molecules in the deposition solution are identical, and since it is clear that only a very small fraction of the molecules on the Au surface are template molecules, it follows that the much longer framework molecules compete more effectively for surface adsorption sites

than the template molecules. This is consistent with results reported by Whitesides and coworkers,¹⁴ and it arises principally from the greater van der Waals interaction potential between the framework molecules.

Figures 1c and 1d are consistent with the qualitative interpretation of Figure 1b. The shapes of these voltammograms arise from spherical diffusion of $\text{Ru}(\text{NH}_3)_6^{3+}$ to small, widely dispersed defect sites on the electrode surface. As the concentration of the template molecules in the deposition solution is increased relative to the framework molecules, the maximum limiting current, i_{lim} , increases, and there is a clear departure from pure spherical diffusion to a mixed linear/spherical regime.^{10,15,19} Mixed diffusion behavior is especially evident in Figure 1e, and when 4-HTP/ C_{16}SH = 15, nearly ideal linear diffusion obtains, Figure 1f.²⁰ When 4-HTP/ C_{16}SH = 30, the cyclic voltammetry obtained using the modified surface, Figure 1g, is indistinguishable from that of a naked Au surface, Figure 1h. The voltammetry shown in Figure 1 does not change significantly even after 10 voltammetric cycles.

Figure 2 presents data analogous to those shown in Figure 1,

Figure 2

except that the solution-phase redox probe molecule is $\text{Fe}(\text{CN})_6^{3-}$. This set of data follows the general trend discussed for $\text{Ru}(\text{NH}_3)_6^{3+}$. For example, there is a clear progression from electron transfer via tunneling through the monolayer film to

direct electron transfer at the electrode surface governed first by spherical, and then by linear, diffusion as the 4-HTP/C₁₆SH ratio increases. Qualitatively, the only difference between the cyclic voltammograms shown in Figures 1 and 2 is that the transition from spherical to linear diffusion occurs at a higher 4-HTP/C₁₆SH value for Fe(CN)₆³⁻ than for Ru(NH₃)₆³⁺. Since the perforated monolayers used to generate Figures 1 and 2 are the same, and since the size of the two probe molecules is approximately the same based on their diffusion coefficients,²¹ there is only one possible explanation for this behavior: some of the defect sites that admit Ru(NH₃)₆³⁺ do not admit Fe(CN)₆³⁻. That is, although the total number and average size of the defects is fixed, there are differences in the nature of the intermolecular interactions between the probe molecules and at least some of the molecular recognition defect sites. This observation indicates that the defect sites discriminate between probe molecules based on their chemical nature.

We have also investigated differences in the electrochemical behavior of perforated, self-assembling monolayers as a function of structurally similar, but chemically distinct, defect-inducing template molecules. Figure 3 presents data that is identical to

Figure 3

those discussed for Figure 1, except that the template molecule is 4-TC (HS(C₆H₄)CH₃). We chose this compound because 4-HTP may form hydrogen bonded, phase separated clusters that increase the size

of the induced defects in an unpredictable way. For example, Bain et al. have suggested that hydroxyl-terminated *n*-alkanethiols will tend to form microscopic, hydrogen-bonded clusters a few tens of angstroms across on the Au surface.^{14d} This conclusion was supported by the rationalization that the energy required to disrupt hydrogen bonding in an alkane environment is high, and it was further supported by experimental data, which showed that alcohols in alkane solvents exist primarily as tetramers.²² Since intermolecular hydrogen bonding between 4-TC molecules can not occur, we anticipate no template aggregation and, therefore, smaller defects within the organic monolayer, compared to the 4-HTP system, for a given template/framework ratio. In addition to differences in the size of the defects, their number is also likely to be a function of the chemical nature of the template molecules. These expectations are borne out; even when 4-TC/C₁₆SH = 30, Figure 3i, spherical diffusion obtains, indicating differences in the size and/or number of defects. We hypothesize that non-hydrogen-bonding species do not compete as effectively for the Au surface as their hydrogen-bonding counterparts, since the latter should have several S/Au binding interactions per defect site. Experiments with other templates, such as 4-mercaptopyridine and 4-mercaptobenzoic acid, are consistent with this view.²³

An effort was made to quantify the data shown in Figure 3 using a theoretical model developed by Amatore et al.¹⁵ They have shown a correlation between the average defect radius and distance between defects, and the resulting cyclic voltammetry response in

a solution of a redox probe molecule. The model is appropriate to the chemical systems described here if the perforated monolayers act as arrays of non-interacting ultramicroelectrodes; that is, if diffusion is hemispherical and if the diffusion layers of the individual ultramicroelectrodes do not overlap. This situation corresponds to Figures 3h-i. In these cases, i_{lim} is related to the fractional surface coverage of $C_{16}SH$, θ , and the average defect radius, R_a , through the relationship given in eq 1. Here, n is the

$$i_{lim} = nFSc^0D(1-\theta)/(0.6R_a) \quad (1)$$

number of electron equivalents, F is the Faraday, S is the geometrically projected surface area of the electrode, c^0 is the bulk concentration of the redox probe molecule, and D is its diffusion coefficient.¹⁵

To directly correlate the calculated and experimental values of i_{lim} , we must know both the size and number density of the defect sites. Unfortunately, we must guess the former and calculate the latter based on the experimentally determined value of i_{lim} .²⁴ Here, we have chosen to analyze the data involving the 4-TC/ $C_{16}SH$ composite monolayer, since we do not anticipate aggregation of the template. That is, we postulate that the minimum radius of a single defect site corresponds to the van der Waals radius of 4-TC, about 3.5 Å, based on its liquid density. The maximum defect size induced by a single template molecule might correspond to the maximum number of n -alkanethiol framework molecules displaced from their three-fold coordination sites on a

Au (111) surface.⁵ This corresponds to a maximum displacement of 7 C₁₆SH molecules, which would open a radius of about 7.5 Å on the surface. For convenience in this approximate calculation, we assume an intermediate average defect radius of 5 Å.

For 4-TC/C₁₆SH ratios of 25 and 30, eq 1 yields 1-θ values of 4.4×10^{-6} and 5.7×10^{-6} , respectively. Viewed differently, this means there are about $10^9/\text{cm}^2$ template-induced defect sites on the electrode surface. This result is on the same order as those obtained by Bilewicz and Majda using L-B methods.¹⁰

CONCLUSIONS

We have shown that it is possible to use binary mercaptan solutions to prepare functional composite monolayers. The chemical nature of the template and the template/framework ratio of the deposition solution control the size, number, and chemical characteristics of the defects. These in turn control access of probe molecules to the Au surface and are therefore responsible for the molecular recognition function of these monolayers. For example, when 4-HTP/C₁₆SH = 15, Ru(NH₃)₆³⁺ easily penetrates the monolayer, but Fe(CN)₆³⁻ does not.

To our knowledge, this is the first example of the use of self-assembly chemistry to construct a binary molecular recognition monolayer composed of simple molecular species, and it is intended to complement strategies based on electrostatic binding,²⁵ covalent bonding,²⁶ hydrogen-bonding,²⁷ and

complexation²⁸ that we have previously reported. We are presently engaged in a thorough analysis of the energetic and spatial relationships between the template, framework, and probe molecules, and those results will be presented in future publications.

ACKNOWLEDGMENTS

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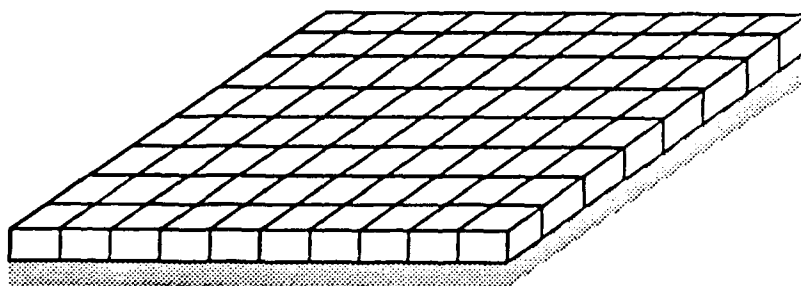
- Wiley: New York, 1974, p. 77. (b) For $\text{Ru}(\text{NH}_3)_6^{3+}$, $D = 7.1 \times 10^{-6} \text{ cm}^2/\text{s}$, see Bard, A. J.; Crayston, J. A.; Kittleson, G. P.; Shea, T. V.; Wrighton, M. S. *Anal. Chem.* **1986**, *58*, 2321.
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FIGURE CAPTIONS

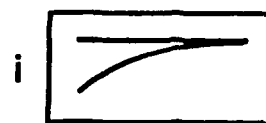
Figure 1. Cyclic voltammograms for perforated, composite monolayers formed by immersing a Au surface in ethanol solutions containing various ratios of 4-HTP/C₁₆SH (HS(C₆H₄)OH/HS(CH₂)₁₅CH₃). The concentration ratio is given above each cyclic voltammogram. The data were obtained in an aqueous electrolyte solution consisting of 5 mM Ru(NH₃)₆³⁺ and 1.0 M KCl.

Figure 2. Cyclic voltammograms for perforated, composite monolayers formed by immersing a Au surface in ethanol solutions containing various ratios of 4-HTP/C₁₆SH (HS(C₆H₄)OH/HS(CH₂)₁₅CH₃). The concentration ratio is given above each cyclic voltammogram. The data were obtained in an aqueous electrolyte solution consisting of 5 mM Fe(CN)₆³⁻ and 1.0 M KCl.

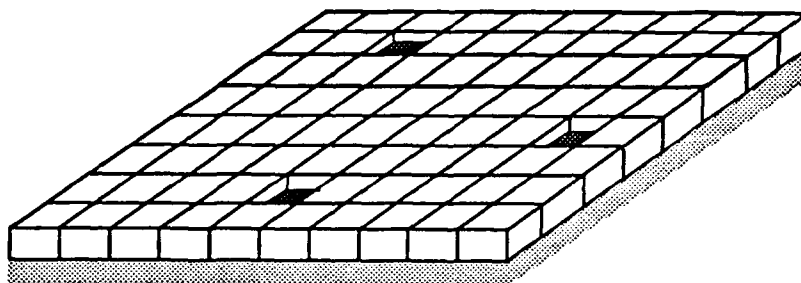
Figure 3. Cyclic voltammograms for perforated, composite monolayers formed by immersing a Au surface in ethanol solutions containing various ratios of 4-TC/C₁₆SH (HS(C₆H₄)CH₃/HS(CH₂)₁₅CH₃). The concentration ratio is given above each cyclic voltammogram. The data were obtained in an aqueous electrolyte solution consisting of 5 mM Ru(NH₃)₆³⁺ and 1.0 M KCl.



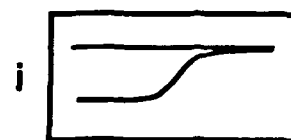
**Framework only
No defects**



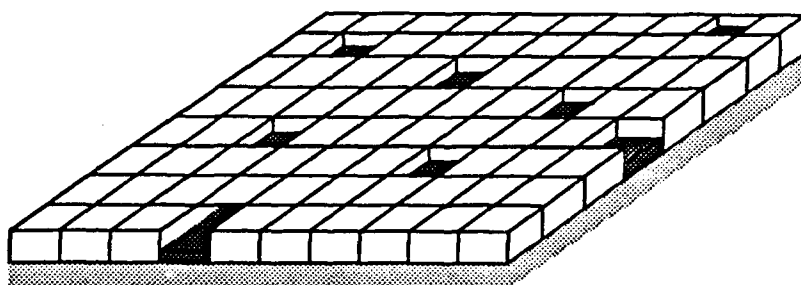
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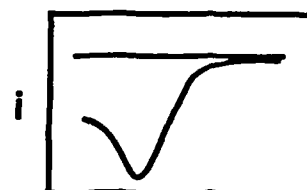
**Low Template / Framework Ratio
Low defect density**



E



**High Template / Framework Ratio
High defect density**



E



= Framework



= Template

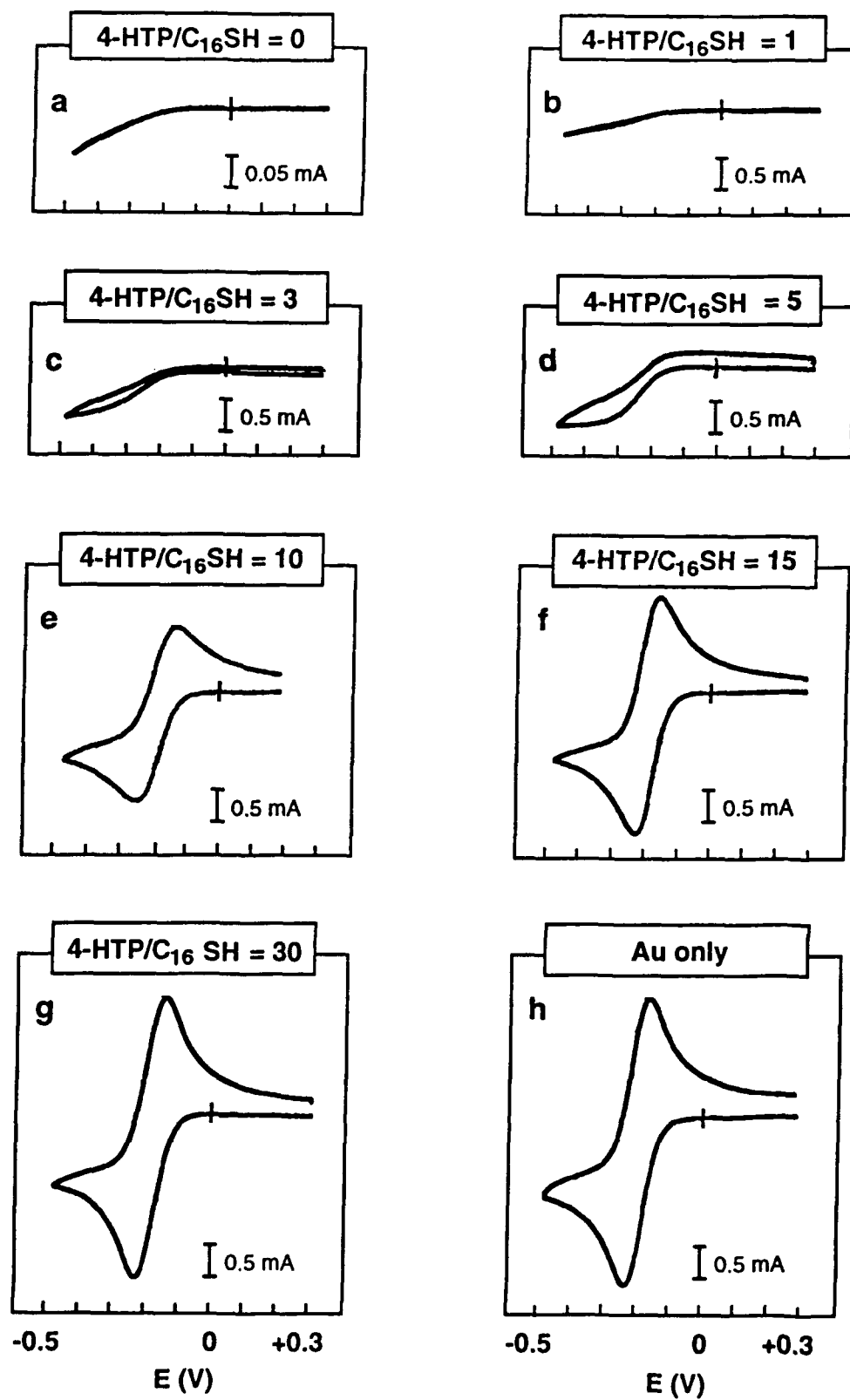


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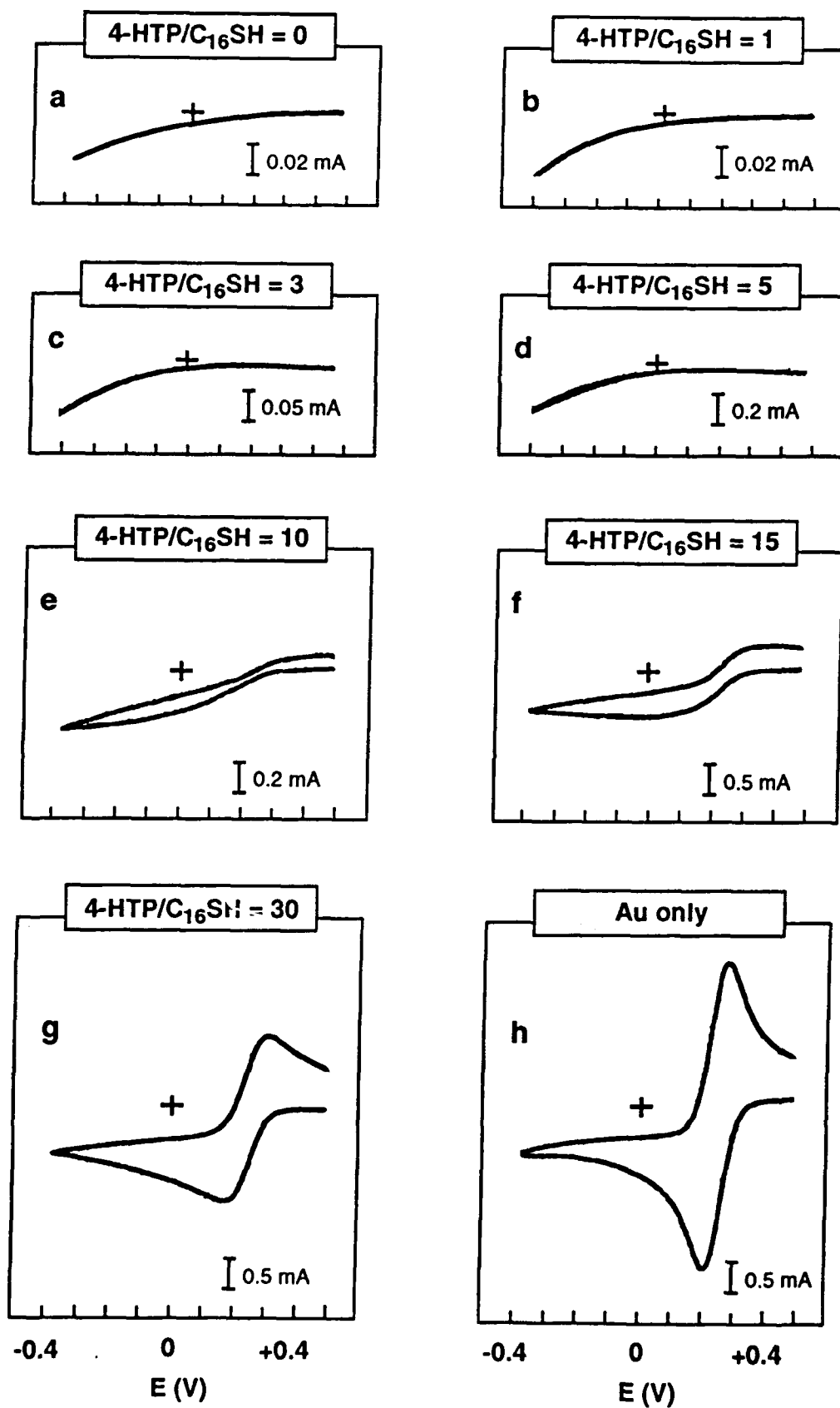


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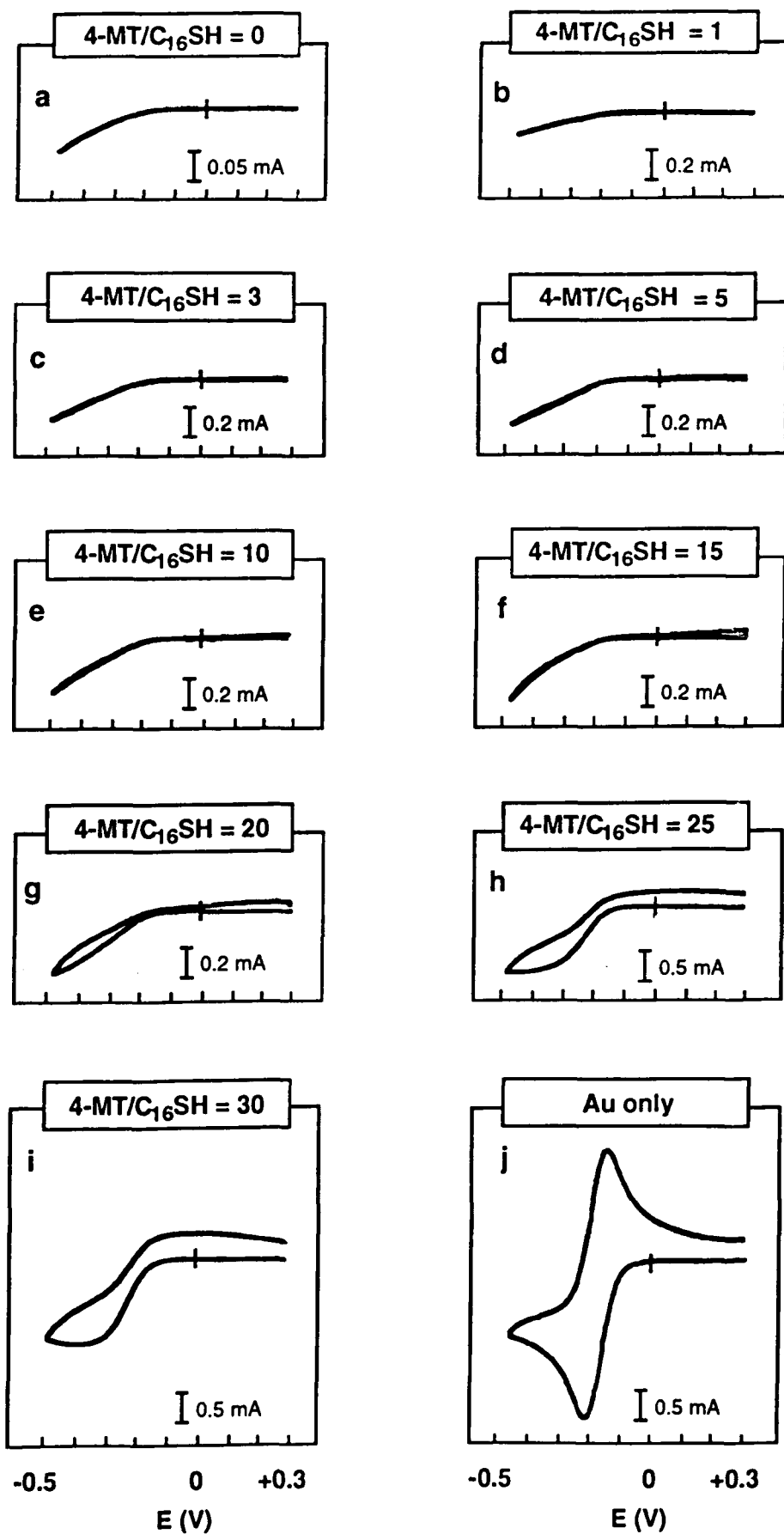


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