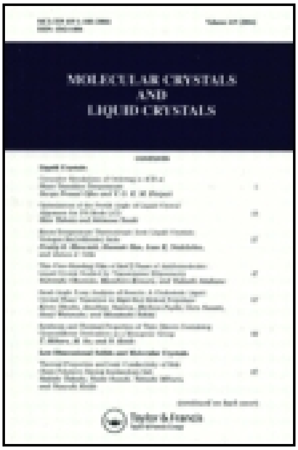

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Self-Assembly Process of Organosulfur Molecular Layers on Gold: Electrochemical Mechanisms

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Self-Assembly Process of Organosulfur Molecular Layers on Gold: Electrochemical Mechanisms

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Mechanism of adsorption process in the self-assembly of organosulfur monolayers on gold was probed by electrochemical measurements. While alkanethiols were found to adsorb on gold by an anodic process, disulfide molecules appeared to adsorb primarily by a cathodic process.

Keywords: self-assembly; monolayer; adsorption mechanism; thiols; disulfides

INTRODUCTION

Interest on the self-assembled monolayers (SAMs) of organosulfur molecules on gold surface has been centered on their structure, properties, and their applications in modification of metal surfaces and functionalization of electrodes, etc.[1-4]. Despite the great interest on SAMs, mechanism of the adsorption process remains to be clarified. Self-assembly on Au from an alkylthiol or from a dialkyl disulfide has been considered by many workers to proceed by chemical steps involving hydrogen production (from thiols) or splitting of the S-S bond (from disulfides) simultaneously with gold-sulfur bond formation as shown below[1-3].

$$\text{RS-H} + \text{Au} \rightarrow \text{RS-Au} + \tfrac{1}{2}\text{H}_2 \qquad (1)$$

$$\text{RS-SR} + \text{AuAu} \rightarrow \text{RS-AuAu-SR} \qquad (2)$$

However, there seems to be little supporting evidence for the adsorption process to occur by the above reactions. To find plausible mechanisms of adsorption and self-assembly of thiol and disulfide molecules, we started electrochemical measurements during the adsorption process. In a previous report[5] we presented results indicating electrochemical reactions involved in the adsorption process. In the present paper adsorption mechanisms of thiols and disulfides involving electrochemical reactions are presented along with more convincing evidences.

EXPERIMENTAL

The electrolyte solution used was 0.10 *M* $LiClO_4$ in acetonitrile, deaerated with purified nitrogen. Either a vacuum-deposited Au slide or a polished gold plate was used as the substrate for SAM formation. In an electrochemical cell, a platinum foil counter electrode and an Ag/AgCl (3*M* NaCl) reference electrode were used. As a small amount of an *n*-alkanethiol ($C_8H_{17}SH$, $C_{12}H_{25}SH$, or $C_{16}H_{33}SH$) or dipropyl disulfide was injected into the solution to 1.0 m*M* concentration, the potential of the gold electrode at the open circuit condition was monitored. Alternatively, at a constant Au potential controlled by a potentiostat, current passing through the electrode was recorded.

RESULTS AND DISCUSSIONS

The open-circuit potential of gold dropped sharply from the initial resting potential on injection of a thiol as shown in Figure 1(A), indicating an *anodic* reaction. A slow upward drift followed the initial drop of potential. Different alkanethiols gave similar results. On the other hand, the potential of gold rose slightly with dipropyl disulfide, indicating a *cathodic* reaction.

When the Au electrode was potentiostatically fixed to an arbitrary potential in the range 0~500 mV, transient currents were observed on injection of the sulfur compounds. As the examples shown in Figure 1(B), the currents were *anodic* in the case of thiols and *cathodic* with the disulfide adsorption. The magnitude and shape of the current peaks depended on the potential chosen. The shifts of electrode potential or the current flows started immediately after the injection of organosulfur compounds as was the ellipsometric signals we reported previously[5]. These findings clearly indicate that the adsorption processes involve electrochemical reactions, instead of the chemical reactions represented by a scheme such as reaction (1) or (2) as in the generally accepted mechanisms.

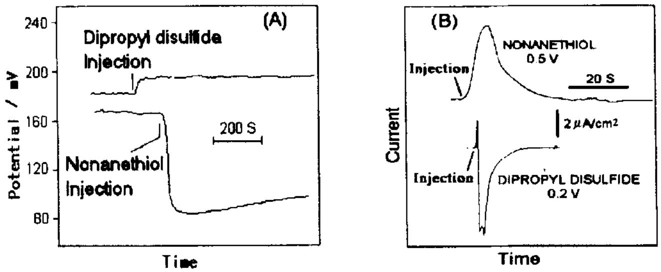

FIGURE 1 Shift of potential (A) of gold and current (B) on injection of hexadecanethiol or dipropyl disulfide.

The anodic current and the negative shift of potential observed with adsorption of thiols can be explained by an *electrochemical oxidation* mechanism:

$$RSH + Au \rightarrow RS\text{-}Au + H^+ + e \qquad (3)$$

When the electrode is left open from the control circuit, the potential of the electrode must change to negative direction with the negative charge accumulating on the gold surface. The capacitance of the gold/electrolyte interface is charged as the potential of gold changes until the potential becomes too low for reaction (3) to proceed further. Undoubtedly the reaction will proceed smoothly when the shifting of potential is prevented by the external control. The open-circuit potential of gold is almost always in the range where reaction (3) is possible initially even after rigorous purging of oxygen from the solution. Rubinstein also reported that the adsorption is faster with potential control than at open circuit conditions[7]. Analogous reversible oxidative adsorption and reductive desorption have been reported for HS-containing cysteine molecules[6]. There have also been reports of reversible desorption of SAM layer at large negative potentials of gold[8, 9] and silver[10].

For SAM formation from disulfide molecules, where the potential shift and currents were in the opposite direction to those with thiol adsorption, we propose the following *cathodic* reaction mechanism:

$$\mathrm{RSSR} \;+\; e^{-}(\mathrm{Au}) \;\rightarrow\; \mathrm{RS\text{-}Au} \;+\; \mathrm{RS}^{-} \qquad (4)$$

A part of RS^{-} ions generated can be adsorbed by an anodic reaction similar to reaction (3), the rest diffusing away into the solution:

$$\mathrm{RS}^{-} + \mathrm{Au} \rightarrow \mathrm{RS\text{-}Au} + e^{-}(\mathrm{Au}) \qquad (5)$$

Although reaction (5) is an anodic reaction the sign of the overall current or the potential shift should be as observed because reaction (4) is predominate. Reduction of a disulfide into two RS^{-} ions as we previously hypothesized[5] is not likely to occur at the usual open circuit potentials. However, reaction (4) is possible due to the strong chemical affinity of sulfur to gold. These mechanisms of adsorption of thiols and disulfides envision possible control of the rate of SAM formation processes and the quality of the films formed. Evidently, the adsorption is facilitated with the potential controlled to suitable ranges, higher for thiols and lower for disulfides, whereas the potential of gold shifts with adsorption when uncontrolled, resulting in hindrance to continuous adsorption.

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