Toward Orthogonal Self-Assembly of Redox Active Molecules on Pt and Au: Selective Reaction of Disulfide with Au and Isocyanide with Pt

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Surfaces of platinum and gold adsorb 12-ferrocenyldodecyl isocyanide, I, and bis[10-(ferrocenylcarbonyl)-decyl] disulfide, II, and yield self-assembled, redox active monolayers incorporating ferrocene groups. The values of $E_{1/2}$ for alkylferrocenyl centers from I are ~300 mV more negative than acylferrocenyl centers from II. This difference allows easy electrochemical measurement of surface concentrations of ferrocene centers from I and II on Pt or Au. I adsorbs selectively on Pt or Au compared to II, but with different degrees of selectivity. Further, for Pt the selectivity depends on the surface pretreatment. The affinity of II for a Pt surface first exposed to an O_2 plasma (oxidized Pt) is lower than that for a Pt surface exposed first to an O_2 plasma and then to a H_2 plasma (reduced Pt), but the two plasma pretreatments of Pt do not affect the binding of I on this metal. The same two plasma pretreatments of Au do not influence the selectivity for binding I vs II; the selectivity for binding I vs II on Au is ~8:1. By use of the O_2 plasma pretreatment and a 40:1 solution of II:I, self-assembly of II onto Au and I onto Pt can be effected when the two samples are derivatized in the same solution.

We wish to report procedures for formation of self-assembled monolayers that modify Au and Pt electrodes selectively when both are immersed in a common solution containing the isocyanide, I, and the disulfide, II, eq 1. Much work has been reported recently concerning the use of self-assembly methods to functionalize electrode surfaces.[1-11] Relatively little work, however, has been reported concerning the self-assembly of multicomponent systems on different substrates. We have named selec-

tivity of the sort represented in eq 1 "orthogonal self-assembly",[12] meaning that each molecule adsorbs selectively to a different surface. We have previously demonstrated such orthogonal self-assembly for Au and Al_2O_3: thiols selectively bind to Au, and carboxylic acids bind selectively to Al_2O_3.[12] Part of the significance of our new findings is that both Pt and Au are useful electrode materials, whereas insulating Al_2O_3 is not. Thus, orthogonal self-assembly using I and II can be exploited to prepare an organized two-component, redox active molecular assembly. A potentially more important application would be to take a single component molecular assembly and use the two different functional groups as "clips" to span the space between two adjacent microelectrodes. Thus, not only would selective functionalization be achieved but also *orientation*.

Self-assembly of redox active monolayers has been accomplished by immersion of Pt and/or Au into organic solutions of I[13] and/or II.[14,15] The $E_{1/2}$ for the alkylferrocenyl centers from I is ~300 mV more negative than $E_{1/2}$ for the acylferrocenyl centers from II, allowing easy electrochemical measurement of their surface concentra-

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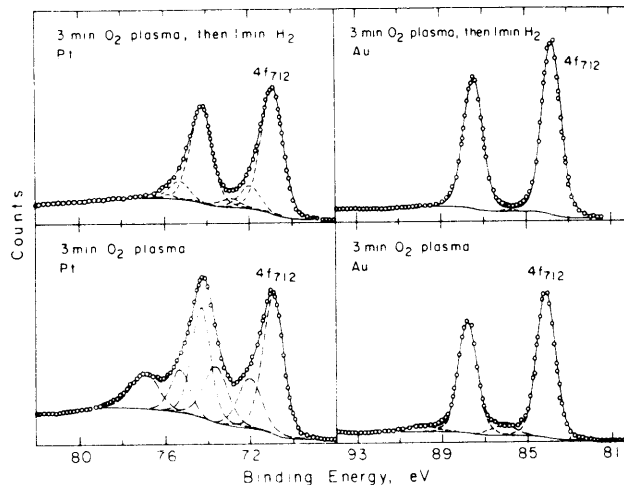(13) The synthesis of I will be published in the full paper detailing this work.
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(15) Prior to derivatization the e⁻-beam evaporated Au and/or Pt on a Si substrate was pretreated with an O_2 plasma (2-5 min) or with the O_2 plasma followed by a H_2 plasma (1 min). Plasma treatment was done using a Harrick PDC-23G plasma cleaner. The O_2 treatment was at 0.3 Torr at medium power (60 W) and the H_2 treatment was at 0.3 Torr at low power (40 W). Immediately after a plasma pretreatment, the electrodes were derivatized by immersion into a deoxygenated 5 × 10⁻⁵ M solution of I or into a 10⁻⁴ M solution of II in 1:1 EtOH/hexane solvent. Best results for orthogonal self-assembly were achieved using the O_2 plasma pretreatment and a 40:1 solution of II:I in 1:1 EtOH/hexane as solvent at total concentration of adsorbate of 10⁻⁴ M. Typical derivatization times were 18-48 h.
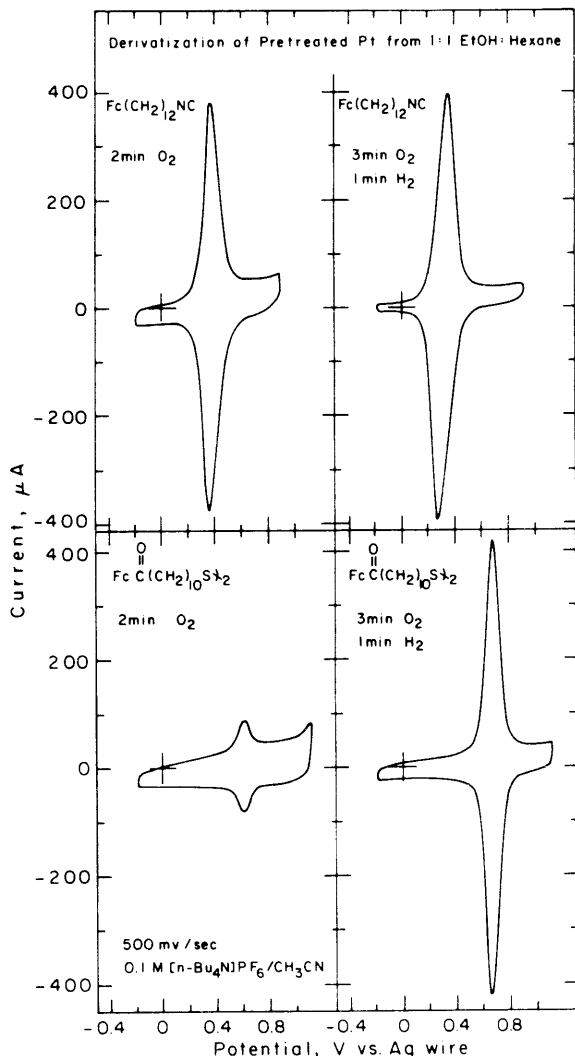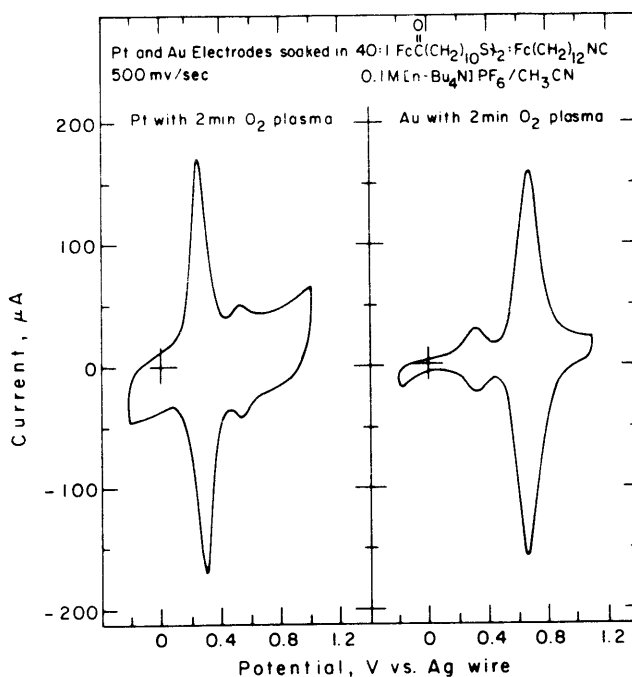
Figure 1. Cyclic voltammetry (500 mV/s) in CH_3CN/0.1 M [n-Bu_4N]PF_6 for Pt electrodes after modification by reaction with 5×10^{-5} M I (top) or with 10^{-4} M II (bottom) for 18 h in EtOH/hexane (1:1). The data on the left are for Pt electrodes pretreated with a 2-min O_2 plasma and the data on the right are for Pt electrodes pretreated with a 3-min O_2 plasma followed by a 1-min H_2 plasma.


Figure 2. Comparison of XPS data for Pt and Au pretreated with a 3-min O_2 plasma or with a 3-min O_2 plasma followed by a 1-min H_2 plasma.

Figure 3. Comparison of cyclic voltammetry (500 mV/s) in CH_3-CN/0.1 M [n-Bu_4N]PF_6 for oxidized (2-min O_2 plasma pretreatment) Pt and Au electrodes after derivatization in EtOH/hexane (1:1) solution containing 1×10^{-4} M II and 2.5×10^{-6} M I for 18 h.

tions even when both species are on the surface. For Au or Pt surfaces pretreated by sequential exposure to an O_2 plasma (2–5 min) followed a H_2 plasma (1 min), we find that I or II form a durable, redox active monolayer ((3–5) $\times 10^{-10}$ mol/cm^2) on either Pt or Au.. However, pretreatment with only the O_2 plasma suppresses the uptake of the disulfide, II, on Pt, while not affecting the uptake of the isocyanide, I, Figure 1. The pretreatment procedure for Au involving only the O_2 plasma gives the same response to I or II as found when pretreatment involves the sequential O_2 and H_2 plasmas. X-ray photoelectron

spectra (XPS) in the $4f_{7/2}$ region, Figure 2, show high binding energy peaks consistent with the presence of a Au or Pt oxide after the O_2 plasma pretreatment which is removed by the H_2 plasma pretreatment.[16]

Ten independent comparisons show that the reduced

$I = R'NC$

$II = RSSR$
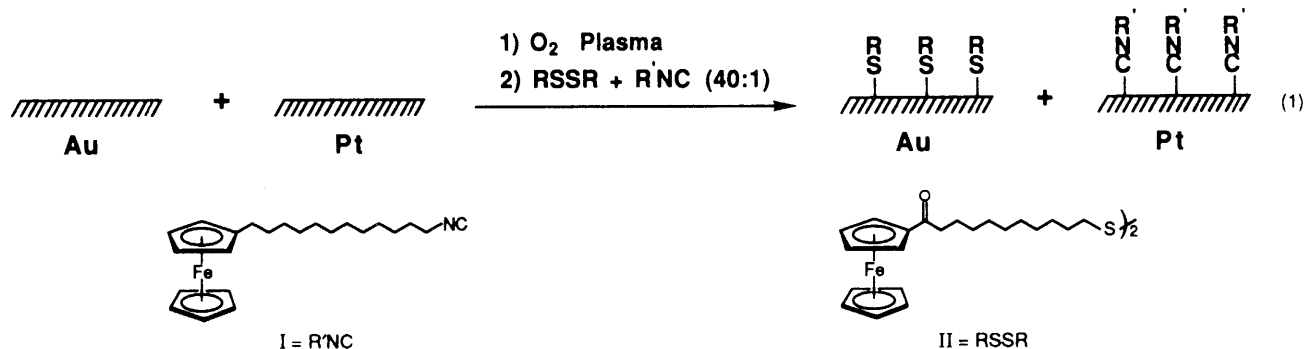
Pt (O_2 plasma followed by H_2 plasma) yields about 10 times the coverage of redox active material as does the oxidized Pt (O_2 plasma only) when reacting both surfaces in the same solution of II, Figure 1. Importantly, oxidized and reduced Pt derivatized with only I show the same coverage, $\sim(4 \pm 1) \times 10^{-10}$ mol/cm^2. XPS analysis of oxidized Pt functionalized with I shows high binding energy Pt $4f_{7/2}$ peaks, consistent with retention of the oxidized surface. In contrast, XPS of oxidized Au after reaction with I or II shows no detectable high binding energy peaks, consistent with loss of the Au oxide. Electrochemically formed Au oxide has also been shown to be reactive toward other surface modification reagents.[17]

Electrochemical analyses of pretreated Pt and Au after reaction with mixtures of I and II show that the isocyanide, I, is always more competitively adsorbed than the disulfide, II, but a sufficiently large ratio of II:I in solution will yield selective uptake of II. The reduced and oxidized Au both give a preference of I vs II of 8:1. Reduced and oxidized Pt, however, have different preferences for I vs II, since oxidized Pt is nearly inert to II. The preferences for uptake of I vs II on oxidized and reduced Pt are ~200:

1 and ~20:1, respectively. Thus, pretreatment of Pt and Au with only the O_2 plasma is predicted to give the highest degree of orthogonal self-assembly by reaction with I and II with Pt and Au.

By using a 40:1 ratio of II:I in solution and the O_2 plasma pretreatment of Au and Pt, we have demonstrated selective functionalization of Pt with I and selective functionalization of Au with II when derivatized in the same solution of I and II. The self-assembly yields a 1:10 and 10:1 ratio of alkylferrocenyl/acylferrocenyl centers on Au and Pt, respectively, Figure 3. The total coverage of ferrocene centers is always $\sim(4 \pm 1) \times 10^{-10}$ mol/cm^2, or about one monolayer. Changing the ratio of I and II in solution changes the ratio of the two different centers on the Au and Pt surfaces in a manner consistent with a competitive reaction of I and II. Further studies are underway to establish the scope of orthogonal self-assembly on Pt and Au, in order to functionalize microelectrode arrays[12,13] with a variety of redox centers.

(16) XPS was done using an SSL 100 spectrometer. Samples were attached to the stage via metal clips. The lowest energy Pt $4f_{7/2}$ peak was taken to be Pt(0) and the lowest energy Au $4f_{7/2}$ peak was taken to be Au(0), and they were monitored as the reference to correct any peak shifts due to sample charging (Au(0) $4f_{7/2}$ is at 84.0 eV and Pt(0) $4f_{7/2}$ is at 71.0 eV binding energy). The X-ray line used for excitation was the Al Kα line at 1486.6 eV. For a general reference, see: *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer Corp.: Eden Prairie, MN, 1979.

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