# Formation and Electrochemical Characteristics of Multilayers of Au Nanoclusters Covered by Mixed Self-Assembled Monolayers of Three Kinds of Alkanethiols with Methyl, Ferrocene, or Carboxylate Terminal Group on Au(111) Surface

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Multilayers of Au nanoclusters covered by self-assembled monolayers containing a mixture of three kinds of alkanethiols terminated by methyl, ferrocene, or carboxylate groups were constructed on a Au(111) surface based on the electrostatic interaction between a carboxylate anion and metal cation. Electrochemical measurements showed that an electron is transferred between ferrocene and the Au(111) electrode through the Au nanocluster cores and/or ferrocene groups.

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The formation of ordered multilayers of metal and semiconductor nanoclusters has attracted significant interest in view of the wide variety of the applications in nanotechnology and nanodevices. Several groups have already successfully formed monolayer and multilayers of metal[1–5] and semiconductor[6–9] nanoclusters on solid surfaces, e.g., using the electrostatic interaction between an anion and cation.[2,3] Although the attachment of the functional groups to the nanoclusters is expected to significantly increase the possible applications of nanocluster assemblies, the multilayer formation of the nanocluster with functionalities have not been reported.

Self-assembled monolayers (SAMs) of alkanethiols on gold have been used as one of the most molecularly ordered layers with functionalities.[10,11] We have already succeeded in introducing ferrocene as an electrochemically active group into the alkanethiol SAM on gold and constructing an electrochemically active surface.[12,13] Since Schiffrin and his coworkers reported the SA technique to protect the Au nanocluster surface,[14] many studies on Au nanoclusters covered by alkanethiol SAMs have been carried out,[1–3,15–20] because of its easy preparation and its high stability. Thus, by combining the multilayer formation of the Au nanoclusters with the introduction of the functional groups into the alkanethiol SAM-protected Au nanoclusters, a nanocluster multilayer with functionalities should be constructed. We have attempted the introduction of the ferrocene moiety into the multilayer of the CdS nanoclusters by post-treatment using ferrocenylalkanethiol after the self-assembly but the ferrocene group was introduced only to the SAM on the gold substrate.[9]

We now report the successful formation of the multilayers of the Au nanoclusters protected by the mixed SAMs with three kinds of alkanethiols containing a methyl, ferrocene, or carboxylate terminal group, based on the electrostatic interaction between carboxylate and metal cation. Electrochemical characteristics of the multilayers of the mixed alkanethiol SAM-protected Au nanoclusters on Au(111) electrodes were investigated.

The hexanethiol ($C_6$) SAM-protected Au nanocluster (average core diameter: 2.4 nm) was synthesized using Schiffrin's method.[14] Ferrocenylhexanethiol ($C_6$Fc) and 11-mercaptoundecanoic acid ($C_{10}$COOH) were introduced into the Au nanocluster surface by the place-exchange method.[19] A molar ratio of $C_6$:$C_6$Fc:$C_{10}$COOH on the Au nanocluster surface was estimated by $^1$H NMR to be 12:16:1. The literature method[2] based on the carboxylate/$Cu^{2+}$/carboxylate electrostatic bridge was used to deposit the mixed SAM-protected Au nanocluster on a gold substrate. Prior to the deposition, a Au(111) substrate (surface area = 0.083 $cm^2$) was modified with a SAM of $C_{10}$COOH in order to construct the carboxylate-terminated substrate. Deposition of the mixed SAM-protected Au nanocluster was carried out by alternate two-step dips of the carboxylate-terminated Au(111) substrate in an ethanol solution containing 1 mM $Cu(ClO_4)_2$ for 2 min and the 0.15 wt% mixed SAM-protected Au nanocluster for 5 min with a rinse cycle.

Figure 1 shows the cyclic voltammograms (CVs) of the carboxylate-terminated Au(111) electrodes, which were prepared by repeating the above two-step dip and rinse cycles for 1, 2, 3, 5, and 10 times, measured in dichloromethane containing 0.1 M tetrabutylammonium perchlorate (TBAP) at a scan rate of 100 mV $s^{-1}$. The oxidation and reduction peaks at +420 mV (vs Ag/AgCl) due to the redox reaction of the ferrocene (Fc)/ferricenium cation ($Fc^+$) couple were observed in all cases. If the dipping of the substrate in the ethanol solution containing $Cu^{2+}$ before the dip in the Au nanocluster solution was omitted, no current peaks were observed, showing that the carboxylate/$Cu^{2+}$/carboxylate electrostatic interaction is essential for the mixed SAM-protected Au nanocluster attachment. The amount of the redox active ferrocene group in adsorbed $C_6$Fc estimated from the anodic charge of the redox peak for the carboxylate-terminated Au(111) electrode prepared by 1 cycle of the two-step dip and rinse was $6.8 \times 10^{-10}$ mol $cm^{-2}$, which is slightly greater than that at the closed-packed $C_6$Fc SAM modified flat gold electrode ($5.5 \times 10^{-10}$ mol $cm^{-2}$).[12] Because this sample was

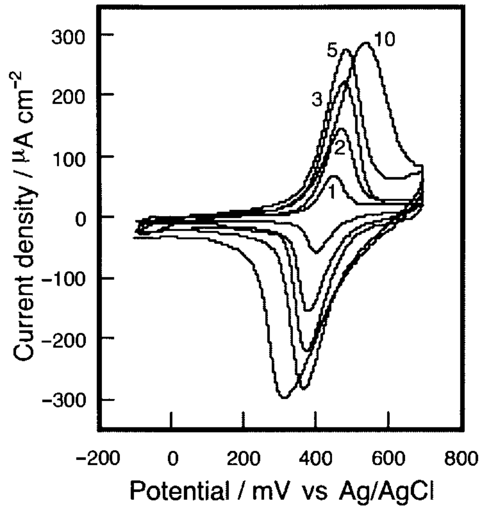

**Figure 1.** Cyclic voltammograms of carboxylate-terminated Au(111) electrode prepared by two-step dips and rinse cycles for 1, 2, 3, 5, and 10 times measured in dichloromethane containing 0.1 M TBAP at a scan rate of 100 mV $s^{-1}$. Number of cycles is described in the figure.

prepared by only one cycle of the above two-step dips and rinse cycle, the mixed SAM-protected Au nanoclusters is expected to be a monolayer. If the alkyl chains of the mixed SAMs are in an extended conformation like that on the flat gold surface, the thickness of the SAM of the longest molecule among $C_6$, $C_6$Fc, and $C_{10}$COOH, i.e., $C_{10}$COOH SAM, should be about 1.0–1.2 nm.[10,11] Thus, the diameter of the mixed SAM-protected Au nanocluster is expected to be ca. 4.4–4.8 nm. If a closely-packed layer of the mixed SAM-protected Au nanoclusters is formed, the number of the Au nanoclusters per one layer is estimated to be $5.5–6.6 \times 10^{12}$ clusters $cm^{-2}$. Because the total amount of the ferrocene groups electrochemically determined is $4.1 \times 10^{14}$ molecules $cm^{-2}$, the amount of adsorbed $C_6$Fc on each Au nanocluster should be 62–74 molecules $cluster^{-1}$. This value is in good agreement with the value estimated from the adsorbed molar ratio (63 molecules $cluster^{-1}$) when 114 alkanethiols were adsorbed onto the surface of the 2.4 nm core diameter Au nanocluster.[19]

The greater the number of alternate two-step dip and rinse cycles, the greater the charge of the redox peaks, showing that multilayers of the mixed SAM-protected Au nanoclusters formed on the carboxylate-terminated Au(111) electrode surface (Figure 2).[21] The amount of charge of the redox peaks linearly increased with the number of cycles up to 3 cycles. The amount of the charge increased further with the cycles but to a lesser degree than that expected for the linear relationship because either the layers formed in the 5th or more cycles were relatively loosely-packed or not all the ferrocene groups adsorbed on the Au nanocluster surface were electrochemically active.

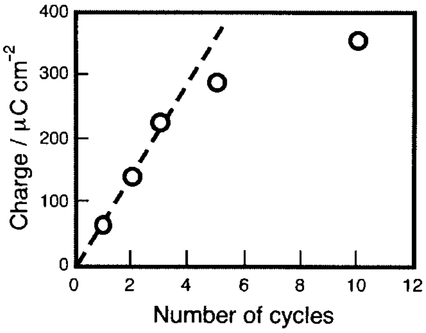

**Figure 2.** Relation between number of cycles of two-step dip and rinse and charge of the redox peaks of CVs in Fig. 1.

Because the core size of the Au nanoclusters is 2.4 nm and the thickness of the SAM is 1–1.2 nm, the distance between the ferrocene group on the Au nanocluster surface in the third layer and the Au(111) electrode should be always more than 10 nm, which is far too long for electron tunneling, and if the Au nanocluster layer is not closely-packed, the distance is larger than that when the layer is closely-packed. Thus, the electron should be transferred between the ferrocene groups and Au(111) through Au nanocluster cores and/or ferrocene groups by hopping as schematically shown in Figure 3.

In conclusion, we have constructed the multilayers of Au nanoclusters covered by mixed SAMs using three kinds of alkanethiols with a methyl, ferrocene, or carboxylate group based on an electrostatic interaction between the carboxylate anion and copper cation by alternate two-step dips in the ethanol solution of 1 mM $Cu(ClO_4)_2$ for 2 min and of the 0.15 wt% mixed SAM-protected Au nanocluster for 5 min with rinse cycles. The amount of adsorbed Au nanoclusters increased with the cycles, linearly up to 3 cycles and then less from 5 cycles. Electrochemical measurements showed that electron is transferred between ferrocene and the Au(111) electrode through the Au nanocluster cores and/or the ferrocene groups.

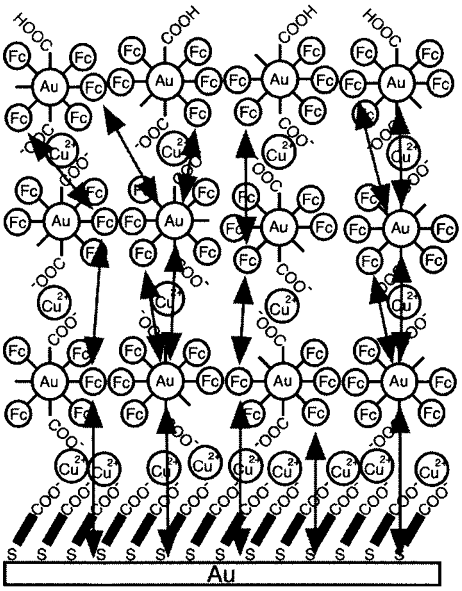

**Figure 3.** Schematic model of electron transfer at the multilayers of the mixed SAM-protected Au nanoclusters formed on the carboxylate-terminated Au(111) electrode. Arrows indicate electron transfer.

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21 We confirmed the step-by-step multilayer formation of the mixed SAM protected Au nanocluster from the absorption spectra data, in which the intensity of the plasmon band (527 nm) increased with the number of the two-step dips and rinse cycles in preparation.