Electroreductive Deposition of Au Clusters Modified with an Anthraquinone Derivative

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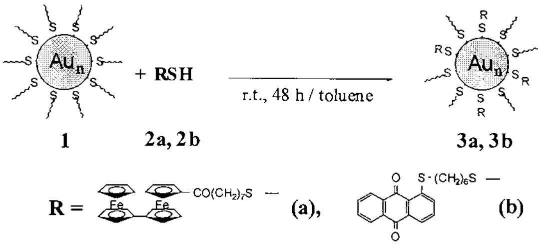
Anthraquinone derivative-modified Au clusters prepared by a substitution reaction of octyl thiolate-covered Au clusters with 1-(1,8-dithiaoctyl)anthracene-9,10-dione undergo a two-step one-electron reduction in aprotic solvents, resulting in the formation of an electroactive thin Au cluster film. Composite film formation is achieved by a combination of oxidative and reductive electrodeposition of biferrocene derivative-modified and anthraquinone derivative-modified Au clusters, respectively.

Nanometer-sized Au clusters possess unusual physical and chemical properties, e.g. a strong surface plasmon band and high catalytic activity, so that a variety of applications to advanced technologies have been extensively investigated.[1,2] In particular, alkyl thiolate-covered Au clusters[3] are stable in air, soluble in nonpolar organic solvents, and furthermore, capable of facile modification with other thiols involving physical and chemical functionality through exchange reactions. Synthesis as well as the electrochemical properties of the Au clusters covered with thiols containing redox-active species such as ferrocene and anthraquinone (AQ) have been reported by Murray and his coworkers.[4-6]

We have recently reported the synthesis and electrochemical behavior of biferrocene derivative (**2a**) -modified Au clusters, **3a**.[7] Electrochemical deposition of the Au clusters occurs when the biferrocene units are oxidized to the biferrocenium (2+) form, resulting in the formation of a stable and adhesive electroactive Au cluster film. Neither the biferrocenium (1+) form of **3a** nor the ferrocenium form of the ferrocene derivative-modified Au clusters are deposited on the electrode surface, suggesting that the local charge accumulation is effective for the electrodeposition.

This phenomenon prompted us to examine the possibility of reductive electrodeposition using Au clusters modified with redox species forming multivalent anions. In this study, we employed AQ derivative-modified Au clusters because a 2- charge can be stored for an AQ moiety. It should be noted that the previous report of an AQ derivative-modified Au cluster does not mention the redox reaction of the AQ^-/AQ^{2-} couple nor the electrodeposition.[6] We have actually found the electrochemical deposition phenomenon of Au clusters modified with a new AQ derivative, 1-(1,8-dithiaoctyl)anthracene-9,10-dione (**2b**). In this paper we report the redox properties and the electrodeposition behavior of the AQ derivative-modified Au clusters, **3b**. We also report the formation of a composite film by the combined oxidative and reductive deposition of **3a** and **3b**, respectively.



Scheme 1.

The starting materials, **1**[3] and **2b**[8] were synthesized on the basis of literature methods. We performed the preparation of **3b** by a thiol-exchange reaction of **1** with **2b** in toluene solution (Scheme 1). TEM images of **1** and **3b** determined that these reaction conditions produced Au clusters of which the average core diameter was 2.2 (± 0.3) nm, corresponding to 309 Au atoms with a cuboctahedron core shape.[9] It has been reported that the number of alkyl thiolate units in one cluster is 95 for this cluster size.[4,5] The number of exchanged AQ-terminated thiolates on the Au cluster surface (θ_{AQ}), which was determined from the ratio of the peak integrals of the proton NMR signals between AQ and methyl, could be controlled by changing the mole ratio of **2b** to **1**. UV-vis spectra of **3b** exhibited a surface plasmon band at 516 nm (ε_{max}=7.7 × 10^5 mol^{-1}dm^{3}cm^{-1}) and additional absorption bands derived from the AQ moiety at 444 nm (ε_{max}=9.1 × 10^5 mol^{-1}dm^{3}cm^{-1}) and 316 nm (ε_{max}=1.3 × 10^6 mol^{-1}dm^{3}cm^{-1}).

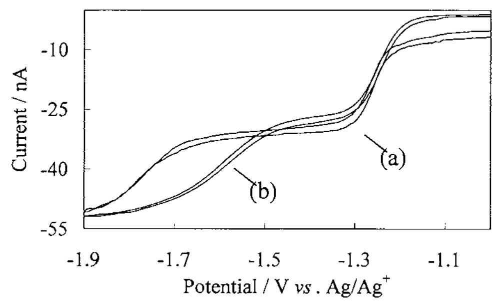


Figure 1. Cyclic voltammograms of **3b** (θ_{AQ} = 26, 27 μmol dm^{-3}) (a) and **2b** (107 μmol dm^{-3}) (b) at a 7 μm-diameter GC disk in 0.1 mol dm^{-3} Bu_4NClO_4-toluene+MeCN (2:1 v/v) at 20 mV s^{-1}.

Table 1. Electrochemical properties of **2b** and **3b** measured by microelectrode voltammetry[a]

Substrate	θ_{AQ}	$E^{0\prime}_1$ / V[b]	$E^{0\prime}_2$ / V[b]	n_1	n_2	$10^6 C_{dl,Au}$ / F cm^{-2} AQ^0	AQ^{-1}	AQ^{-2}
2b	-	-1.21	-1.54	1.0	0.49	-	-	-
3b	10	-1.23	-1.66	1.0	0.70	7.2	9.4	27
3b	18	-1.23	-1.70	1.0	0.49	8.0	12	29
3b	26	-1.22	-1.74	1.0	0.47	16	32	71

[a] In 0.1 mol dm^{-3} Bu_4NClO_4-toluene+MeCN (2:1 v/v). [b] *vs.* Ag/Ag$^+$

Cyclic voltammograms of both **2b** and **3b** at a 7 μm-diameter GC microelectrode in Bu_4NClO_4-toluene+MeCN (2:1 v/v) show a two-step 1 e$^-$ reduction with the limiting current (Figure 1). The electrochemical behavior of AQ is known to be sensitive to the measurement conditions.[10] We investigated how the reduction behavior of the free AQ derivative, **2b** would be altered by fixing the derivative to the Au cluster surface, and the results are given in Table 1. The table indicates that the number of electrons transferred per AQ radical anion n_2 is smaller than unity for both **2b** and **3b**. The second reduction potential $E^{0}{}'_2$ of **3b** was shifted in the more negative direction than that of **2b**. The magnitude of this potential shift is larger for the clusters with higher θ_{AQ} (Table 1), suggesting that the second reduction of the AQ moiety at the Au cluster surface is strongly affected by the interaction between the adjacent AQ moieties. The double-layer capacitance of **3b**, $C_{dl,Au}$ estimated from the slope of the limiting currents increases with the accumulation of negative charge on the AQ moiety, namely, $C_{dl,Au}(AQ^0) < C_{dl,Au}(AQ^-) < C_{dl,Au}(AQ^{2-})$.

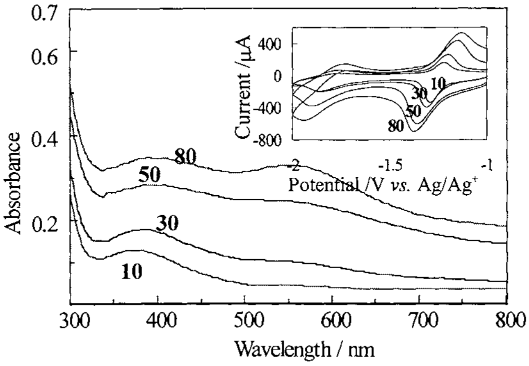


Figure 2. UV-vis spectra of electrodeposited films of **3b** at ITO. The inset shows the cyclic voltammograms of the films in 0.1 mol dm^{-3} Bu_4NClO_4-MeCN at 0.1 V s^{-1}. Numbers in the figure refer to the number of cyclic scans.

The electrodeposition of **3b** was examined by cyclic voltammetry using an indium-tin oxide (ITO)-coated glass electrode. Consecutive potential scans between –1.0 and –2.0 V *vs*. Ag/Ag$^+$ in a solution of **3b** in the same electrolyte solution as noted above caused a gradual increase in the peak current. The cyclic voltammogram of the electrode thus treated in pure electrolyte solution without **3b** exhibits a redox reaction at $E^{0}{}' =$ -1.26 and –1.81 V *vs*. Ag/Ag$^+$, as shown in the inset of Figure 2. Its UV-vis spectrum shows broad absorption bands, which grow with increases in the number of cyclic scans for electrodeposition (Figure 2). These results denote the formation of electroactive thin Au cluster films on the ITO electrode. The previous results for biferrocene derivative-modified Au clusters, **3a** and the present results indicate that the surface local charge accumulation is the cause of the electrodeposition. We deduce that the charge accumulation increases the local ionic strength and thus compacts the ionic atmosphere around the cluster particles, resulting in a decrease in electrostatic repulsion between the particles. Consequently, the van der Waals force between adjacent Au clusters near the electrode becomes dominant, and an aggregation of the cluster particles takes place.

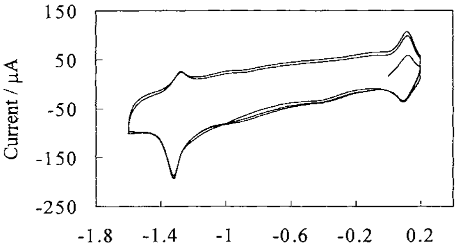


Figure 3. Cyclic voltammogram of a composite film of **3a** and **3b** at ITO in 0.1 mol dm^{-3} Bu_4NClO_4-MeCN at 0.1 V s^{-1}. The film was prepared by 15 cyclic potential scans between –0.3 and 0.9 V vs. Ag/Ag$^+$, 15 scans between –1.0 and –2.0 V, and again 15 scans between –0.3 and 0.9 V, in a mixed solution of **3a** ($\theta_{\text{biferrocene}} = 8.3$, 7.2 μmol dm^{-3}) and **3b** ($\theta_{AQ} = 26$, 4.0 μmol dm^{-3}) in 0.1 mol dm^{-3} CH_2Cl_2 at 0.1 V s^{-1}.

UV-vis spectra of the films of **3b** show a broad band at *ca.* 560 nm of which the intensity increases when the electrodeposition proceeds (Figure 2). This band is regarded as the surface plasmon band, which is known to be sensitive to the local dielectric medium around metal clusters.[11] It can be deduced that the interparticle spacing becomes small compared to the incident wavelength, and a new feature corresponding to a collective Au cluster surface plasmon oscillation grows as the cluster coverage increases.[12]

We next carried out an attempt to prepare composite films by combining both the electrooxidative deposition of **3a** and the electroreductive deposition of **3b**. Figure 3 shows a cyclic voltammogram of the film coating of ITO when the potential cycling between –0.3 V and 0.9 V for the redox reaction of **3a** and between –1.0 and –2.0 V for the reaction of **3b**, and again between –0.3 and 0.9 V was carried out 15 times in a solution of the mixture of **3a** and **3b** in Bu_4NClO_4-CH_2Cl_2. Redox activity of both biferrocene and AQ can be observed, indicating the formation of a composite Au cluster film. This combined electrodeposition system would be profitable for arranging high-dimensional hetero-networks of metal clusters. The details of this composite film formation are presently under investigation in our laboratory.

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