The Preparation and Electrochemical Behavior of Density-controlled Gold Nano-particle Self-assembled Interface

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(Received November 8, 2004; CL-041323)

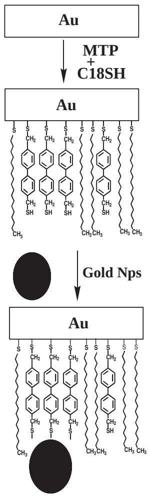
A simple method is described for fabricating gold nanoparticle-modified electrode (NP/SAM/gold), on which the density of NPs on the interface can be controlled by altering SH-terminated thiol abundance in the SAM.

Adsorption of organic thiols on metal surfaces, especially on gold surface, which gives a highly ordered monolayer known as a self-assembled monolayer (SAM) has been studied extensively over the past decade.[1] SAMs are particularly important because of various potential applications in, for example, molecule electron devices and the preparation of optoelectronic nanodevices. Considerable attention has been paid to the formation and characterization not only of unitary (single-component) but also binary (a mixture of two components) self-assembled monolayer films on gold surface.[2,3] Compared with pure unitary SAMs, mixed SAMs might offer a means of overcoming several problems, such as the high densities of surface functional groups which lead to steric hindrance, and less ordered structures due to bulk terminal groups produced by adjusting the abundance, type, and spatial distribution of tail groups.[3] Several studies have shown that mixed SAMs may promote protein adsorption due to the multiple chemical functionalities on the surface and the decrease in steric effects.[4]

Gold nanoparticle-modified electrodes have received considerable attention in recent years.[5,6] They have been intensively investigated in biomolecule electron transfer and analytical applications, etc. Because gold NPs are strongly adsorbed on the SAM surface of SH-terminated thiols, the binary SAMs of fixed SH-terminated thiols and CH_3-terminated alkanethiols are expected to provide a surface which can control NP adsorption on the nanometer-scale domain.

In this paper, we demonstrate a simple method for fabricating gold NP modified electrode (NP/SAM/gold), on which the density of NP on the interface can be controlled by altering SH-terminated thiols abundance in SAMs. 4,4′-bis(sulfanylmethyl)biphenyl (MTP), rigid rod dithiols, form assemblies in which one thiol group binds to the surface, while the other thiol moiety projects upward at the exposed surface of the SAM.[7] There was no indication of in-looped structures in which both thiol ends were adsorbed to the surface, which may occur in flexible, long chain alkanedithiols. The binary SAMs was formed by MTP and 1-octadecanethiol (C18SH) molecules coadsorbing simultaneously on gold electrode surface.

Scheme 1 shows the procedure for preparing density-controlled gold nanoparticle self-assembled interface. The method for preparing gold NPs and modified interface was the same as that in previous report.[8] Because gold NPs were adsorbed only on the –SH terminal group, the density of gold NPs in the SAM depended on the composition of the monolayer and the distribution of the MTP. The composition of the binary monolayer was changed by varying the ratio, $c_{\mathrm{C18SH}}/(c_{\mathrm{MTP}} + c_{\mathrm{C18SH}})$, of MTP and C18SH in the solution. The preferential adsorption of gold nanoparticles on MTP molecules was confirmed by SEM images. Examples of SEM images of gold NPs in the interface are shows in Figure 1. As we see in Figure 1, the density of gold nanoparticles decreases in the relation to the increase in the mole fraction of C18SH in mixed solution. From the SEM images, it was found that the distribution of gold NPs on the binary SAM was not uniform. This was due to the phase-separated binary SAM of MTP and C18SH formed from the mixed solution. The average size of gold NPs was 7.2 ± 2.2 nm in diameter.



Scheme 1. The modification procedure.

$Fe(CN)_6^{3-/4-}$ redox couple was chosen as an electrochemical indicator because of its electrochemically reversible outersphere one-electron redox reaction in aqueous systems. Figure 2 shows the typical cyclic voltammograms obtained in 2 mM ferricyanide solution. At bare gold electrode, the peak current increases linearly with the square root of the scan rate from 0.01 to 4 V/s, as we can see in Figure 2a, and the $E^{0'} = 237$ mV (vs AgCl/Ag) values remain constant when the scan rate is changed, indicating that the process is controlled by linear diffusion. Redox currents of the ferricyanide almost completely disappear after adsorption of MTP and/or C18SH (without gold NPs), as we can see in Figure 2b. This implies that high cover-

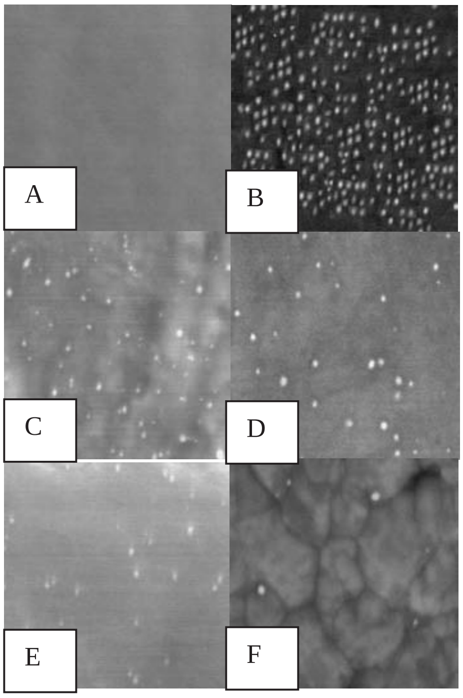


Figure 1. High-magnification (100,000×) SEM images of gold NPs/SAM/Au formed by coadsorption of MTP and C18SH followed by adsorption of gold nanoparticles. The total concentration of thiols in mixed solution was $1.0 \times 10^{-3}\,\mathrm{mol{\cdot}dm^{-3}}$ and the concention (mM) of MTP was A:0; B:1.0; C:0.25, D:0.1; E:0.05; F:0.02. The dimensions of the images are $500 \times 500\,\mathrm{nm}$.

age and packing density of the dithiol monolayer was formed on the gold electrode and the electron transfer was hindered. However, the redox current of the ferricyanide was restored after the modification of the Au electrode adsorbing gold NP.

Figure 2c shows the CV response of the NPs/SAM/Au electrode in 2 mM $\mathrm{Fe(CN)_6}^{3-}$ solution. The peak separation (ΔE_p) is 68 mV and $E^{0'} = 234\,\mathrm{mV}$ at potential scan rate 10 mV/s. At low scan rate, the cyclic voltammograms obtained on the electrode were nearly the same as those obtained on bare gold electrode (Figure 2a). The experimental results show that gold NPs adsorbed on the interface act as tiny conduction centers (electron antenna) and promote electron transfer between electroactive species and the electrode.[5] In other words, each gold NP can be regarded as a nanoelectrode and the interface acts as nanoelectrode arrays. It is known that the voltammetric response at an array of nanoelectrode depends on experimental time scale (e.g., potential scan rate), the shape of the electrode element and the distance between the elements. At low potential scan rate (long time scale), the diffusion layer of each electrode element would have entirely overlapped, voltammograms were peak shaped, and peak current increased with the square root of potential scan rate. With increasing potential scan rate, the diffusion layer changed from an entirely overlapping to a partial overlapping and lastly to a nonoverlapping region, and the voltammograms evolved from a peak shape to a sigmoidal form. The turnover point is related to the distance between each electrode element. For high density gold NP-modified electrode (short distance between each element), sigmoidal shape voltammograms can be observed at high scan rate, while sigmoidal shape forms are obtained on low density gold NP-modified electrode (long distance between each element) at low scan rate. Figures 2c and 2d compares cyclic voltammograms obtained at density-controllable gold NP-modified electrode. As expected, the voltammograms change from a peak shape to a sigmoidal shape with increasing potential scan rate.

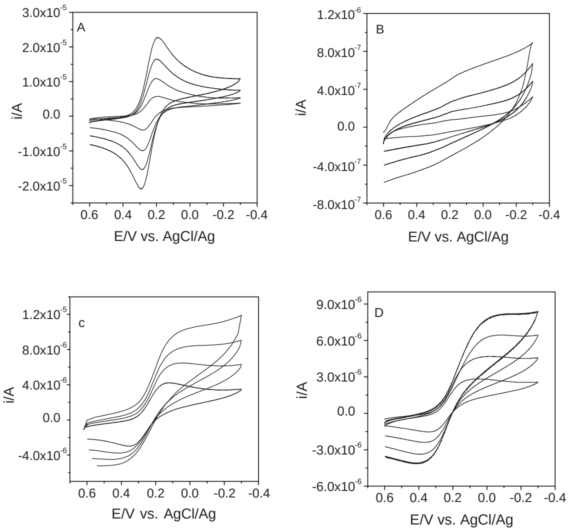


Figure 2. Cyclic voltammograms of 2 mM ferricyanide in 0.5 M KCl. Sweep rates for increasing peak currents: 10, 40, 100, 200 mV/s. A: bare Au electrode; B, C, and D are the same as A, E, and F in Figure 1, respectively.

In summary, we have demonstrated a simple approach for the fabrication of density-controllable gold NP-modified electrode. It should be added that C18SH acted as diluent alkylthiolates in this experiment, but if functional group-terminated thiols are used instead of C18SH, for example, thioctic acid,[9] gold NP-modified electrode with a peculiar micro-environment and microstructure may be obtained. This may be useful in investigations of protein electron transfer and such studies are currently in progress in our laboratory.

This work was partially supported by the Epson International Scholarship Foundation. B. Jin thanks Nature Science of Anhui Province of China.

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Published on the web (Advance View) January 29, 2005; DOI 10.1246/cl.2005.302