# Monitoring of the Transfer of Tetrachloroaurate(III) Ions by Thin-layer Electrochemistry and Electrochemical Deposition of Metallic Gold over a Graphite Electrode

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This study demonstrates the electrochemical conversion of the synthetic procedure of monolayer-protected clusters using a thin toluene layer over an edge plane pyrolytic graphite electrode. A thin toluene layer with a thickness of 0.31 mm was coated over the electrode and an immiscible liquid/liquid water/toluene interface was introduced. The transfer of the tetrachloroaurate ($AuCl_4^-$) ions into the toluene layer interposed between the aqueous solution and the electrode surface was electrochemically monitored. The $AuCl_4^-$ ions initially could not move through into the toluene layer, showing no reduction wave, but, in the presence of the phase transfer reagent, tetraoctylammonium bromide (TOABr), a cathodic wave at 0.23 V *vs.* Ag/AgCl was observed, indicating the reduction of the transferred $AuCl_4^-$ ions in the toluene layer. In the presence of dodecanethiol together with TOABr, a self-assembled monolayer was formed over the electro-deposited metallic gold surface. The FE-SEM image of the surface indicates the formation of a highly porous metallic gold surface, rather than individual nanoparticles, over the EPG electrode.
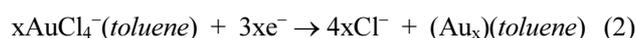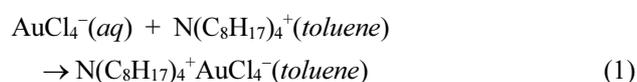
**Key Words :** Liquid-liquid interface, Thin layer electrochemistry, Phase transfer, Tetrachloroaurate ion, Electro-deposition

## Introduction

The surface morphology of an electrode is related to the electrochemical activities of some compounds. For example, different glucose oxidation behaviors were observed at gold electrodes having different surface states after various pre-treatments,[1,2] or at platinum electrodes with meso- or nano-porous surfaces.[3,4] Electrocatalytic effects on nano-electrodes, in comparison to bulk electrodes, are an important issue.[5-7] The size effects of nanoparticles have also been reported, indicating that the surface morphologies are important in elctrocatalytic oxidations of compounds such as carbon monoxide, methanol, and formic acid.[8-11] Hence, systematic studies are required to produce suitable surface morphologies, such as micro- or nano-structures, and obtain an understanding of their correlated effects on catalytic electrode reactions.

In constructing nano-structures on electrode surfaces, several studies of the attachments or electrochemical formations of gold nanoparticles were reported.[12-19] Monolayer-protected cluster (MPC) molecules, which have the advantages of easy isolation, solubility in common organic solvents without aggregation, and versatile functionalization and derivatization, have been extensively studied and their electrochemical properties were reported.[20] The preparation of MPCs suggested by Schiffrin and coworkers includes the formation of thiol-derivatized gold nanoparticles in a two phase liquid-liquid system.[21] The tetrachloroaurate(III) ($AuCl_4^-$) ions are transferred from an aqueous phase into a toluene phase using tetraoctylammonium bromide (TOABr) as the

phase transfer agent and reduced by aqueous sodium borohydride (Eqs. 1 and 2).[21]

$$AuCl_4^-(aq) + N(C_8H_{17})_4^+(toluene)$$
$$\rightarrow N(C_8H_{17})_4^+ AuCl_4^-(toluene) \qquad (1)$$

$$xAuCl_4^-(toluene) + 3xe^- \rightarrow 4xCl^- + (Au_x)(toluene) \quad (2)$$

In the presence of the alkyl-thiol (RSH) in the toluene phase, thiol-derivatized gold nanoparticles are produced (Eq. 3).[21]

$$xAuCl_4^-(toluene) + yRSH(toluene) + 3xe^-$$
$$\rightarrow 4xCl^- + (Au_x)(RSH)_y(toluene) \qquad (3)$$
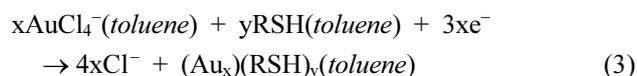
In this system, the source of electrons is the $BH_4^-$ ions. In the present study, we used the electrons from the electrode instead of those from the chemical species in the heterogeneous aqueous/toluene/electrode system, as indicated in Figure 1, and the reactions corresponding to Eqs. (2) or (3) proceeded electrochemically. The movement of the $AuCl_4^-$ ions between the aqueous and organic phases was electrochemically tested and the role of the phase transfer agent was also confirmed. Metallic gold was electrochemically deposited on the electrode surface, rather than remaining in the solution phase, and the surface morphology was investigated.

Immiscible thin organic layers between electrode surfaces and aqueous solutions were introduced in order to make use of their different characteristics in comparison to those of conventional solution/electrode surface systems.[22-26] They
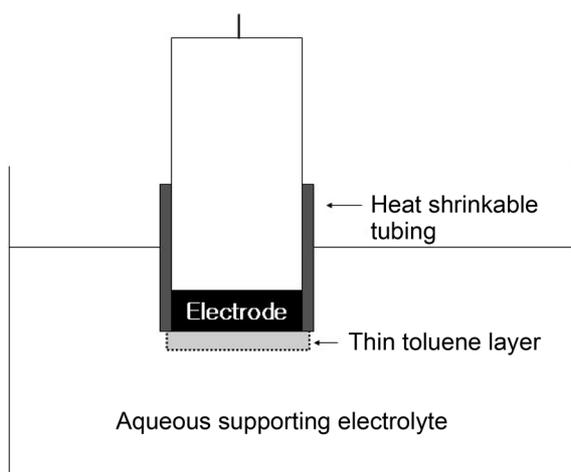
**Figure 1**. Schematic depiction of the EPG electrode with a thin toluene layer between the electrode surface and aqueous supporting electrolyte.

allow some electrochemical measurements, which are normally not possible or at least complicated, to be made possible or simplified. Using the liquid/liquid interfaces, the electron transfer rate constants between two redox reactants were easily estimated[24,25] and the proton transfer across the liquid/liquid interface was electrochemically monitored.[26] The present system employs an immiscible toluene layer between an aqueous solution and an electrode surface (Figure 1), which has a similar structure to the reported one,[24-26] and the transfer of $AuCl_4^-$ ions was monitored electrochemically.

## Experimental

**Materials.** Commercial reagent grade chemicals were used as received. Hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4 \cdot 3H_2O$), sodium bromide (NaBr, 99%), toluene ($C_6H_5CH_3$, 99.8 %) and 1-dodecanthiol ($CH_3(CH_2)_{11}SH$, 99%) were purchased from Aldrich. Tetraoctylammonium bromide (TOABr, $C_{32}H_{68}NBr$, 99%) was purchased from Fluka. Deionized water purified by passage through a purification train (Human Power II$^+$, Human Co.) was used for the preparation of solutions.

For the working electrode, an edge plane pyrolitic graphite (EPG) disk rod (geometric area, 0.32 cm$^2$) was placed on stainless steel shafts and wrapped with heat shrinkable polyolefin tube (Alpha wire Co.). The surface of the electrode was ground using 600 and 1200 SiC papers, sonicated, washed with deionized water, and dried in air. An appropriate amount of a toluene aliquot was dropped over the EPG surface to form an organic thin layer as in Figure 1.

**Apparatus and procedures.** The electrochemical measurements were carried out using a model CHI 630 electrochemical analyzer (CH-Instruments, Austin, TX) controlled through a personal computer. A two-compartment cell was used. The cell had a teflon cap through which the electrodes and a gas bubbling system were fitted. A working electrode and a platinum auxiliary electrode were situated in one compartment, which was separated by fritted glass from the other compartment where the Ag/AgCl reference electrode was held. The potentials were read and quoted with respect to the Ag/AgCl (3 M NaCl) reference electrode with a potential of 0.22 V *vs*. NHE. The supporting electrolyte was 0.1 M NaBr and argon gas was used to remove the oxygen from the solution. All experiments were carried out at room temperature (22 ± 1 °C).

Field emission scanning electron microscopy (FE-SEM) images were obtained using a Hitachi model S-4700 instrument provided by the Korea Basic Science Institute at Chonju.

## Results and Discussion

**Electrochemical monitoring of the movements of $AuCl_4^-$ ions through a thin organic toluene layer.** An EPG electrode, which was prepared by the procedure described in the experimental section, was employed to obtain the cyclic voltammogram in the aqueous 0.1 M NaBr supporting electrolyte, as shown in Figure 2. The voltammogram with the bare EPG electrode exhibited background charging currents, as shown in Figure 2-a. When a 10 $\mu$L aliquot of pure toluene was dropped over the surface of the EPG electrode surface, a uniformly distributed thin toluene layer with a thickness of 0.31 mm was introduced between the aqueous solution and the electrode, as shown in Figure 1, and, with this electrode, another voltammogram with a negligible background current close to zero was obtained, as shown in Figure 2-b. The thin toluene layer over the EPG electrode did not allow the ionic species to move from the aqueous solution phase to the electrode surface, and the charging of electrons inside of the electrode was thereby thought to be inhibited, resulting in negligible current being measured. This result indicates that the toluene layer, which is immiscible with the water solvent, successfully blocked any ionic movements within the supporting electrolyte from the aqueous solution phase to the electrode surface. The
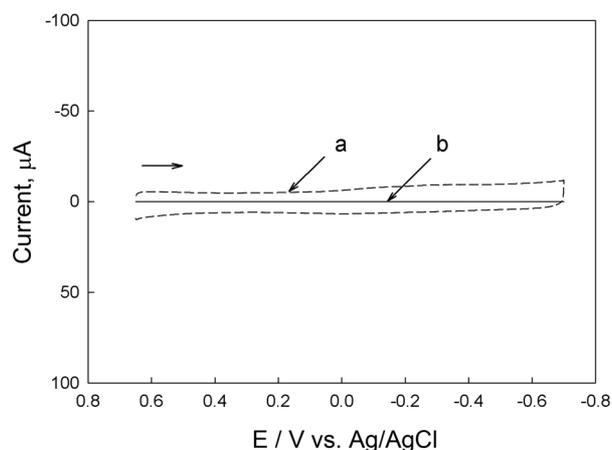


**Figure 2**. Cyclic voltammograms in pure supporting electrolyte at the EPG electrode (a) without (dashed) and (b) with 10 $\mu$L pure toluene coating (solid). Supporting electrolyte: 0.1 M NaBr. Scan rate: 50 mV/sec.
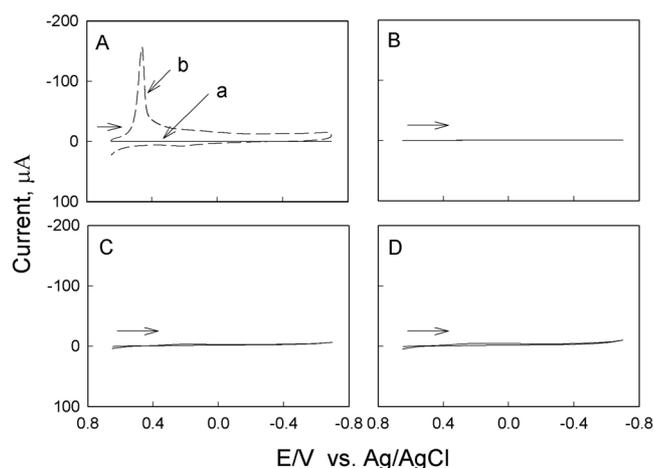
**Figure 3**. Cyclic voltammograms in 0.1 mM HAuCl₄ solution at the EPG electrode coated with 10 μL toluene. The voltammograms were obtained at (A-a) 05 , (B) 10, (C) 30, and (D) 40 min after the toluene aliquot was dropped over the electrode surface. The dashed voltammogram (3A-b) obtained at the bare EPG electrode is shown for the comparison. The other conditions are the same as those in Figure 2.



**Scheme 1**. Schematic descriptions of the transfer of tetrachloroaurate ($AuCl_4^-$) ions into the thin toluene layer and electro-reduction.

thickness of the layer was controllable with the amount of the adding toluene. If the thickness of the layer is not thick enough, the blocking effect would not be perfect. On the other hand, adding too much amount of the liquid toluene did not form an appropriate thin layer.

The voltammograms in Figure 3 were obtained in 0.1 mM HAuCl₄ solution at the EPG electrode coated with a toluene layer and the blocking effect against $AuCl_4^-$ ions was also observed. The measurement time was counted from the moment of addition of the toluene aliquot. The electrode was then quickly immersed into the cell solution and the first voltammogram (Figure 3A-a) was obtained 5 min after the starting point of the measurement and no reduction of the $AuCl_4^-$ ions was observed. When a bare EPG electrode without the toluene layer was used for the purpose of comparison, the $AuCl_4^-$ ions were easily reduced and a large cathodic wave was obtained at a potential of 0.46 V, as shown in the dashed voltammogram of Figure 3A-b. More voltammograms at the electrode coated with the toluene layer were obtained at 10, 30, and 40 min (Figure 3B-3D). Up to 40 min, almost no current change was measured, and, after 40 min, only a slight increase of the current was observed, as shown in Figure 3D. Until about 30 min, the organic toluene layer satisfactorily blocked the transfer of the $AuCl_4^-$ ions from the aqueous solution phase to the electrode surface. After 40 min, however, a slow and gradual increase of the reduction currents were measured as a limited number of $AuCl_4^-$ ions were reduced. This might be because the toluene was slowly absorbed into the inside of the many micro-pores of the EPG electrode and the toluene layer became thinner, thus causing some fraction of the surface to be directly exposed to the aqueous phase, thereby allowing the $AuCl_4^-$ ions to be reduced.

If tetraoctylammonium bromide (TOABr) is contained in the organic layer, the hydrophobic alkyl chain parts of the
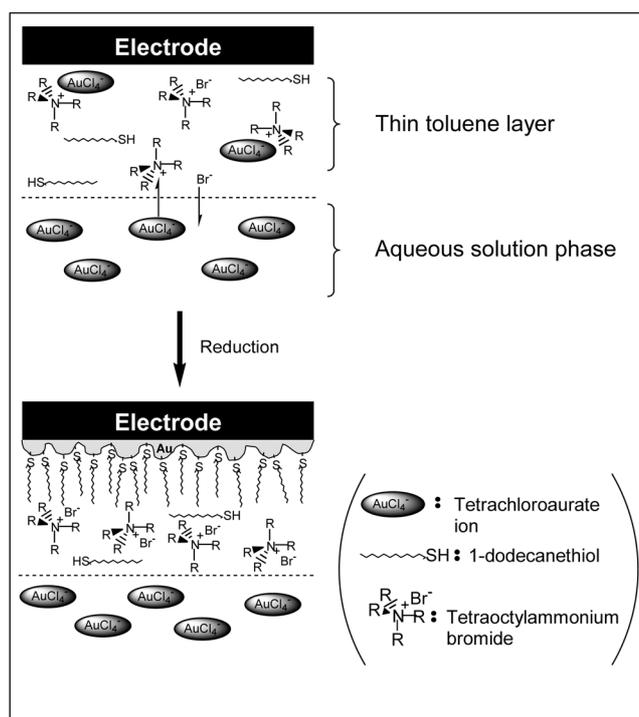
$TOA^+$ cations make them easily soluble in the toluene solvent and the other hydrophilic cations may form ion-pairs with the $AuCl_4^-$ anions by the electrostatic interactions. Hence, in this case, the $AuCl_4^-$ ions can move through the toluene layer with the assistance of the $TOA^+$ ions and would be electrochemically reduced at the electrode surface. In the presence of the thiol compound together with the TOABr, a self assembled monolayer (SAM) would be
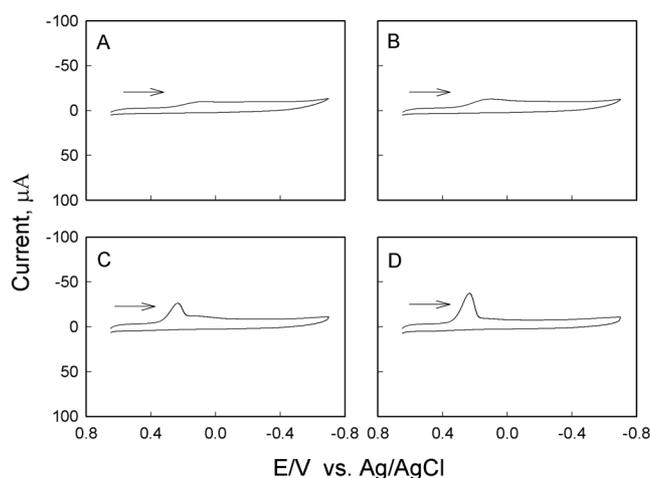


**Figure 4**. Cyclic voltammograms in 0.1 mM HAuCl₄ solution at the EPG electrode coated with 10 μL toluene containing 0.05 M TOABr. The voltammograms were obtained at (A) 05, (B) 10, (C) 25, and (D) 35 min after the toluene aliquot was dropped over the electrode surface. The other conditions are the same as those in Figure 2.

formed on the metallic gold surface electrodeposited on the EPG electrode. This corresponds to the electrochemical conversion represented by reactions 1 through 3, and the process is schematically shown in Scheme 1. Figure 4 shows the voltammograms obtained in 0.1 mM HAuCl$_4$ solution at an EPG electrode on which an aliquot of 10 $\mu$L of toluene containing 0.05 M TOABr (without the thiol compound) was coated. The voltammograms were obtained at 5, 10, 25, and 35 min from the moment when the toluene aliquot was dropped over the surface as in the experiments of Figure 3. In comparison to Figure 3, higher background currents were measured, which was due to the higher charging currents afforded by the TOA$^+$ or Br$^-$ ions in the toluene layer (compare Figure 3A-a and Figure 4A). The cathodic wave at 0.23 V which gradually increases with time (Figure 4B-4D) is considered to correspond to the reduction of the AuCl$_4^-$ ions in the toluene layer. The TOABr acted as a phase-transfer reagent allowing the AuCl$_4^-$ ions to transfer from the aqueous supporting electrolyte to the organic toluene layer. The observed reduction potential of 0.23 V was more negative than the value of 0.46 V at the bare EPG surface, indicating that a higher energy was required to reduce the AuCl$_4^-$ ions in their ion-pair forms in the toluene phase. If a thicker toluene layer is employed, the response in the reduction of the AuCl$_4^-$ ions is expected to be more delayed.

**Electro-deposition of AuCl$_4^-$ ions in the thin toluene layer in the presence of TOABr plus dodecanethiol.** Figure 5 shows the voltammograms obtained in 0.1 mM HAuCl$_4$ solution with an EPG electrode on which an aliquot of 10 $\mu$L of toluene containing 0.05 M TOABr plus 10.4 mM dodecanethiol was dropped. The voltammograms were obtained at 5, 10, 25, and 35 min from the moment when the toluene aliquot was dropped over the surface. In comparison to those in Figure 4, clear larger cathodic waves were observed at 0.20 V. For example, at 35 min, cathodic peak
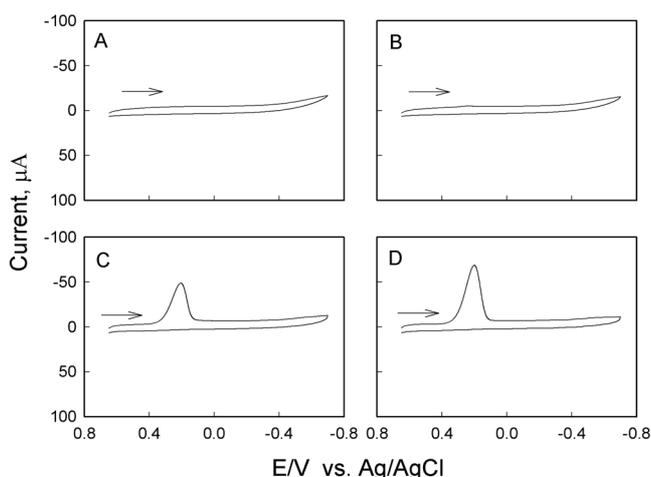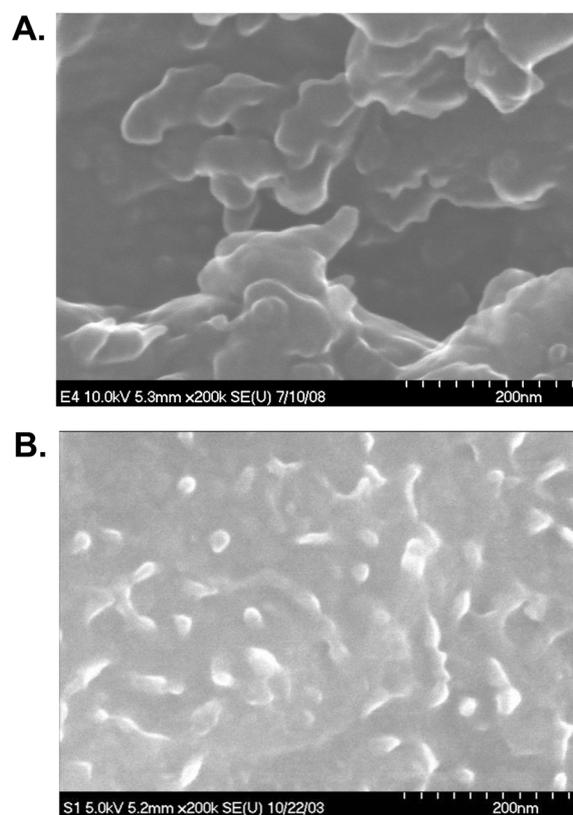


**Figure 6**. The FE-SEM images of the electro-deposited metallic film on the EPG surface. The samples were prepared by scanning the potential from 0.65 V to −0.7 V in 0.1 mM HAuCl$_4$ solution with the EPG electrode, over which an aliquot of 10 $\mu$L of toluene containing 0.05 M TOABr was coated. In the toluene layer, the dodecanethiol was absent for (A) and present for (B). After 7 cyclic scans at 5 min intervals, the electrode was taken out of the cell, washed with methanol, and dried to obtain the images.

currents of 37 $\mu$A and 69 $\mu$A without and with dodeca-nethiol in the toluene layer were measured, as shown in Figures 4D and 5D, respectively. The higher cathodic wave due to the different reduction rate in the presence of dodecanethiol is not clearly understood at this stage. The thiol monolayer formation may stabilize the gold formed on the electrode and facilitate the reduction of the AuCl$_4^-$ ions. Alternatively, the concentration of transferred AuCl$_4^-$ ions in the toluene layer may be increased by the presence of dodecanethiol.

**FE-SEM images of the electro-deposited gold surfaces over the EPG electrode.** The FE-SEM images of the electrode surfaces obtained under the same conditions as those of Figures 4 and 5 are shown in Figure 6. The images shown in Figures 6A and 6B correspond to the cases without and with the dodecanethiol in the toluene layer, respectively. After the AuCl$_4^-$ ions were reduced, the electrodes were taken out of the cell, washed with methanol, dried, and used to obtain the images. In the images of Figure 6, rough metallic gold surfaces were formed. In Figure 6A, without the dodecanethiol in the toluene layer, the gold spots grew horizontally resulting in flat panel shapes and, in the other image of Figure 6B, with the dodecanethiol present, round



**Figure 5**. Cyclic voltammograms in 0.1 mM HAuCl$_4$ solution at the EPG electrode coated with 10 $\mu$L toluene containing 0.05 M TOABr plus 10.4 mM dodecanethiol. The voltammograms were obtained at (A) 05, (B) 10, (C) 25, and (D) 35 min after the toluene aliquot was dropped over the electrode surface. The other conditions are the same as those in Figure 2.

spots with smaller sizes of 20 nm to 30 nm were formed. The presence of the dodecanethiol seems to lead to the formation of gold spots with a different surface structure for reasons, which are not clear yet. Unlike the synthesis of MPCs in the solution phase,[21] individual nanoparticles were not formed. Instead, very rough thin gold films having nano-structures were observed over the EPG surface.

## Conclusions

This study illustrates the successful use of a thin toluene layer to monitor the transfer process of $AuCl_4^-$ ions dissolved in an aqueous phase into an immiscible organic layer coated over an EPG electrode. The $AuCl_4^-$ ions, in the aqueous phase, which normally could not move into the toluene layer, thus giving no electrochemical reduction wave, were able to move into the toluene layer containing the phase transfer reagent, TOABr. The $AuCl_4^-$ ions formed ion pairs with the $TOA^+$ cations, which rendered them soluble in the organic layer and were then electrochemically reduced, showing a well developed cathodic wave. FE-SEM images of the surfaces prepared under these conditions were obtained, showing a highly nano-porous structure rather than the individual nanoparticles, which were previously reported in the literature for MPCs.[21] When the dodecanethiol was present during the formation of the gold surface, round shaped spots with smaller sizes were observed.

Various parameters, such as the concentration of chemical reagents and the way in which the potential is applied, may affect the gold surface nano-structure, and a more precise method of controlling these parameters needs to be established in future studies. As already indicated, the electrode reactions of some electro-active compounds are dependent on the surface structures, which may contain different sized-pores or particles, and catalytic effects were also reported.[1-7] The electrodes developed in this study may be employed to verify the existence of such catalytic effects on the electrode reactions.

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