

Preparation of Nanoelectrode Ensembles by Assembly of Nano-Silver Colloid on Gold Surface

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Abstract: A novel method for preparing silver nanoelectrode ensembles (SNEEs) and gold nanoelectrode ensembles (GNEEs) has been developed. Silver colloid particles were first absorbed to the gold electrode surface to form a monolayer silver colloid. N-hexadecyl mercaptan was then assembled on the electrode to form a thiol monolayer on which hydrophilic ions cannot be transferred. The SNEEs was prepared by removing thiol from silver colloid surface through applying an AC voltage with increasing frequency at 0.20 V (vs. SCE). Finally, GNEEs was obtained by immersing a SNEEs into 6 mol/L HNO_3 to remove the silver colloid particles. By comparison with other methods such as template method *etc.*, this method enjoys some advantages of lower resistance, same diameter, easy preparation, controllable size and density.

Keyword: Nanoelectrode ensembles, microelectrode, silver colloid, self-assembled monolayers.

Composite electrodes not only couple the advantages of single microelectrode systems such as small RC time constant which allows high-speed voltammetry, low ohmic (iR) drops, high rates of mass transport of electroactive species and high signal-to-noise ratio *etc.*, but also with significantly high currents due to larger surface areas¹. Composite electrodes can be divided into two categories, one is uniform (array) dispersions type such as interdigitated ultramicroarray electrode², the other is random (ensemble) dispersion type³. As we know, there are many methods for preparing composite electrode such as imbedding, coating, drawing, lithography⁴ and template method⁶ *etc.* The latter two have been more widely used. Lithography method includes micromachined lithography⁴ and photolithography methods⁵. The size of electrode of the first one is more than 10 microns, the latter can lower the size of electrode to hundreds of nanometers. But it is difficult to prepare more small size of composite electrodes. Template method is a new method which appeared in the recent years. Aluminum oxide or other materials was as template to prepare microelectrode ensembles. Bard *et al.* deposited Au into the pores of polycarbonate membrane filters to prepare nanodisk electrode ensembles⁷. In the large range of unit electrode's dimension is its advantage, but the complicated procedures limit its application. In this paper, we suggest a new method to prepare NEEs by using the assembly of silver colloid and thiol molecules.

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Experimental

Apparatus and reagents

Electrochemical measurements were performed by using CHI660A (Chenhua Instrument Corporation, Shanghai). Chemical cell consisted of three-electrode system. Scanning electron microscope (Philips XL-30) was used to investigate the assembly of silver colloid on the gold electrode surface.

Pretreatment of gold electrode

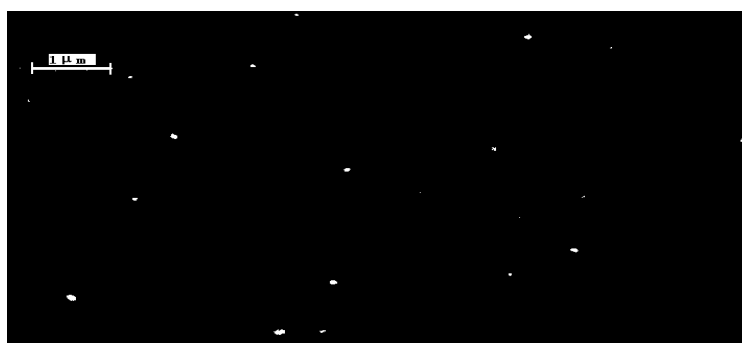
Gold electrodes (diameter of 1.0 mm) were first polished with abrasive paper and then with 3, 0.3 and 0.05 μm alumina respectively and then cleaned in turn by sonications in acetone, diluted nitric acid and water. The peak-to-peak separation of CV with the gold electrode should be less than 70 mV in 0.10 mol/L KNO_3 containing 1.00×10^{-3} mol/L $\text{K}_3\text{Fe}(\text{CN})_6$ at 100 mV/s.

Assembly of monolayer silver colloid and monolayer thiol

The gold electrode was placed in fresh prepared silver colloid⁸ for 4-11 h at 25°C. The obtained monolayer silver colloid was shown in **Figure 1**. It was stored in double distilled water.

Silver colloid modified gold electrode was put into 1.0×10^{-3} mol/L dodecyl mercaptan/alcohol solution for 3-5 h for the assembly, then rinsed with anhydrous ethanol for 15 min to remove redundant thiol.

Figure 1 SEM micrograph of silver colloids adsorbed on gold electrode surface prepared by depositing gold vapor on glass slice



Removal of thiol from silver colloid surface and silver colloid particles from gold electrode surface

The modified gold electrode was put into 0.1 mol/L KNO_3 . The potential was controlled at the 0.20 V (vs. SCE) with adding AC voltage with increasing frequency from 1 Hz to 100 KHz and voltage amplitude of 0.2 ~ 0.3 V to remove the hexadecyl mercaptan monolayer from the silver colloid surface.

Silver nanoelectrode ensembles was immersed in 6.0 mol/L HNO_3 for 2 h for removing the silver colloid particles and Au nanoelectrode ensembles was obtained.

Results and discussion

Monolayer silver colloid on the gold electrode surface

The gold electrode was placed into silver colloid solution directly for the assembly of silver colloid, controlling temperature and immersing time for adjust coverage of silver colloid. When the time was fixed at 5 h, deposition temperature of 5 °C, 25 °C and 40 °C were tested. No Ag/AgCl redox peak could be found on the gold electrode surface when at 5 °C, indicating that no or very small amount of silver colloid was deposited on Au surface. But at 25 °C, the CV graph showed a distinct redox peak of Ag/AgCl. Further increase of peak current occurred at 40 °C. These demonstrate that temperature had great impact on the deposition of silver colloid. A linear relationship existed between the quantity of silver colloid and immersing time when it was less than 5 h (25 °C). When the immersing time of 5 ~ 11 h, silver colloid monolayer was formed on the gold electrode surface. Negative charge surrounding the silver colloid made colloid particles expel each other, and were hard to agglomerate. When the immersing time was longer than 11 h, a multilayer silver colloid was formed.

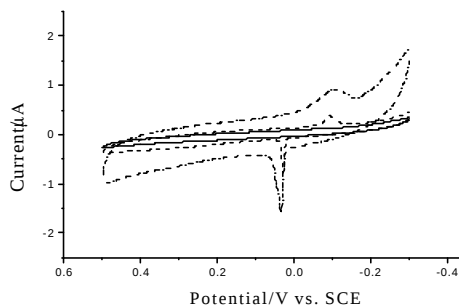
As the Cl^- concentration increases by a factor of 10, the peak potential shifted toward negative about 59 mV and currents increased significantly. But there was no cathodic wave in saturated KCl solution because of dissolution of AgCl to form AgCl_2^- . Redox wave of Ag/AgCl was used here for confirming whether Ag colloids attached to the Au surface or not and to calculate the coverage of silver colloid.

Self-assembly of hexadecyl mercaptan on the surface of gold electrode

Self-assembly of mercaptan at Ag colloid modified electrode was performed in $1.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ hexadecyl mercaptan for 3 ~ 5 h. The redox waves of Ag/AgCl in $0.10 \text{ mol}\cdot\text{L}^{-1}$ KCl disappeared (**Figure 2**), indicating all surface of Ag colloid were covered with mercaptan. The same result occurred in $1.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ $\text{K}_3\text{Fe}(\text{CN})_6$ in the potential range of -0.2 ~ 0.5 V (**Figure 3**), demonstrating all surface of Au were sealed tightly with mercaptan. It is noticeable that there was a couple of redox wave of $\text{K}_3\text{Fe}(\text{CN})_6$ with a hexadecyl mercaptan SAMs of Au electrode as a consequence of defects in SAMs known as pinholes⁹. One can remove the pinholes from SAMs with prior assembly monolayer of silver colloid. Hexadecyl mercaptan on Ag colloids could be selectively removed at 0.20 V by adding AC voltage with increasing frequency from 1 Hz to 100 KHz and voltage amplitude of 0.2 ~ 0.3 V while this process did not affect SAMs on Au. This could be confirmed by cyclic voltammetry in $0.1 \text{ mol}\cdot\text{L}^{-1}$ KCl as the redox waves of Ag/AgCl occurred again (**Figure 2**). Thus, the silver nanoelectrode ensembles were obtained. It can be concluded that we can remove the thiol molecules from silver colloid surface but not from gold electrode surface with this method. The electrode were further treated with $6.0 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 for resolving Ag colloid, we also obtained the Au nanoelectrode ensembles which showed Sigmoidal wave on cyclic

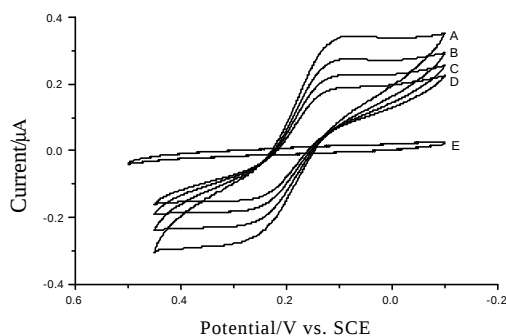
voltammograms in $1.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1} \text{ K}_3\text{Fe}(\text{CN})_6$ (Figure 3).

Figure 2 The Cyclic votammograms of silver colloid modified gold electrode



Modified god electrode in 0.1 M KCl solution (dash dot line), modified gold electrode cover with thiol monolayer (solid line), modified gold electrode after it was processed by Alternating Current Impedance (dash line). Scan rate: 100 mVs^{-1} .

Figure 3 Cyclic voltammograms of gold nanoelectrode ensembles in $1 \times 10^{-3} \text{ mol/L K}_3\text{Fe}(\text{CN})_6 + 0.1 \text{ mol/L KNO}_3$ solution for different scan rate.



A: 100 mVs^{-1} B: 80 mVs^{-1} C: 60 mVs^{-1} D: 50 mVs^{-1} E: The CV of silver colloid modified gold electrode covered fully by *n*-hexadecyl mercaptan in $1.0 \times 10^{-3} \text{ mol/L K}_3\text{Fe}(\text{CN})_6 + 0.1 \text{ mol/L KCl}$ solution.

References

1. H. X. Ju, H. Y. Cheng, H. Gao, *FENXI HUAXUE*, (*Anal. Chem.*, chn), **1992**, 20 (1), 107.
2. E. C. Adam, R. K. Roderick, *Sensors and Actuators B*, **2000**, 62, 23.
3. R. M. Blanchard, A. R. Noble-Luginbuhl, R. G. Nuzzo, *Anal. Chem.*, **2000**, 72 (7), 1365.
4. A. B. Frazier, C. H. Ahn, M. G. Allen, *Sens. and Actuators A*, **1994**, 45 (1), 47.
5. R. V. Zhelyaskov, T. E. Milne, F. J. Hekte, D. M. Morris, *Appl. Spectrosc.*, **1995**, 49 (12), 1793.
6. G. Buss, M. J. Schoning, H. S. Luth, *Electrochim. Acta*, **1999**, 44 (21-22), 3899.
7. V. P. Menon, C. R. Martin, *Anal. Chem.*, **1995**, 67, 1920.
8. I. D. G. Macdonald, W. E. Smith, *Langmuir*, **1996**, 12, 706.
9. G. Timp, *Nanotechnology*, Springer-Verlag New York, Inc., **1999**, p.337.

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