



ELSEVIER

Microelectronic Engineering 66 (2003) 91–94

MICROELECTRONIC
ENGINEERING

www.elsevier.com/locate/mee

Electrochemical study of 4-ferrocene thiophenol monolayers assembled on gold nanoparticles

Di Li, Yuanjian Zhang, Jinghong Li*

*State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, Changchun 130022, China*

Abstract

In this paper, 4-ferrocene thiophenol was employed as a novel capping agent to synthesize electroactive gold nanoparticles. Transmission electron microscopy showed an average core diameter of 2.5 nm. The optical and electrochemical properties of the 4-ferrocene thiophenol capped gold nanoparticles were characterized by UV–Vis spectroscopy and cyclic voltammograms. Surface plasmon absorbance was detected at 522 nm. Cyclic voltammograms revealed the adsorbed layer reaction controlled electrode process, and the formal potential of electroactive ferrocene centers shifted anodically compared with ferrocene in solution, which could be attributed to the electron-withdrawing phenyl moiety linked to ferrocene.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Self-assembled monolayers; Gold surface; Nanoparticles

1. Introduction

Ferrocene is a prototypical redox group that has been frequently incorporated at the terminal site of alkanethiol derivatized self-assembled monolayers (SAMs) on various electrodes [1,2] to study interfacial charge-transfer reactions depending on variables such as reaction driving force, distance, bridging groups and the local microenvironment. However, these studies were mostly focused on fc-SAMs on flat Au surface (2D-SAMs) until Murray et al. [3] reported gold nanoparticles capped by *n*-octanethiolates and ω -functionalized ferrocenyl octanethiolates mixed monolayers (C_8SH/C_8Fc mixed MPCs), which extended the study of Fc-SAMs to three dimensions. In their experiment, the ferrocene moiety was place-exchanged onto the MPCs. Herein we aim to synthesize gold nanoparticles capped by 4-ferrocene thiophenol ligand. Compared with alkanethiolate-MPCs [4] and thiophenol-MPCs [5], the peculiar π -conjugated structure of the monolayers may have some

*Corresponding author. Fax: +86-431-526-2243.

E-mail address: lijingh@ciac.jl.cn (J. Li).

significant effects on the clusters and thus may lead to great application potential in fields such as nanodevices, biosensors and molecule catalysts.

2. Experimental

The nanoparticles were synthesized following a slightly modified Brust reaction [6]. Briefly, 0.5 mM tetrachloroauric acid was reduced by 5 mM sodium borohydride in the presence of 4-ferrocene thiophenol. The crude product was washed with excess amount of water, ethanol and acetone to remove excess thiol and disulfide byproducts. All these reactions were carried out at room temperature.

3. Results and discussion

Fig. 1 shows the TEM image of gold nanoparticles with an average core diameter of ~ 2.5 nm. The number (n) of gold atoms in each cluster can be calculated by assuming the core shape was truncated octahedral and dividing the mass of 2.5-nm gold core by mass of per Au atoms; the calculated results were 490. In addition, a brief calculation indicated that ~ 150 Au atoms were on the surface of the cluster, with 80 Fc-ligands in each cluster [4,7].

Fig. 2 shows an illustrative cyclic voltammograms (CV) of the gold nanoparticles. The single wave of CV indicates all the redox centers of gold nanoparticles appear identical. In addition, the formal potential ($E^{0'} = \frac{E_{pa} + E_{pc}}{2}$) of the gold nanoparticles was 0.5 V as constant with the scan rate and it shifted anodically compared with 0.4 V of C_8SH/C_8Fc mixed MPCs [3].

The formal potential of Fc-SAMs shifts to substantially more positive potential as electron-withdrawing substituents are added to the cyclopentadienyl [8]. In the present study, the positive shift in formal potential could be attributed to the conjugated structure of 4-ferrocene thiophenol.

On the basis of hexagonal close-packing of 2.5-nm MPCs, a full coverage of MPCs monolayer should be 1.67×10^{-11} mol/cm². The absorbed Fc was calculated as 2.06×10^{-10} mol/cm² by integrating the charge under the oxidation wave in CVs. In the present study where 80 Fc ligands were

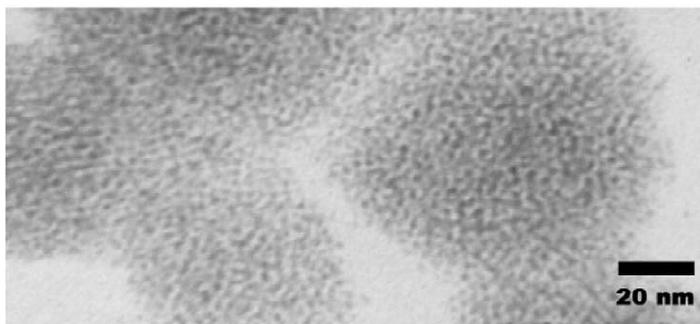


Fig. 1. TEM image of the 4-ferrocene thiophenol capped gold nanoparticles.

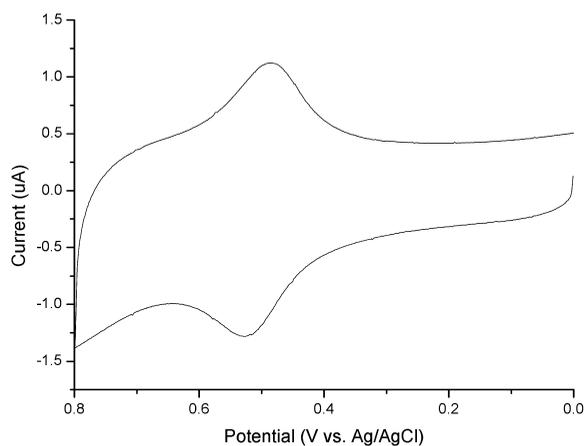


Fig. 2. Cyclic voltammograms of the electroactive gold nanoparticles at glassy carbon electrode in mixed solvent (2:1 toluene:acetonitrile, v/v). The electrolyte was 0.1 M Bu_4NClO_4 . Scan rate, 50 mV/s.

assembled onto each MPC, adsorbed MPCs can be calculated as $2.57 \times 10^{-12} \text{ mol/cm}^2$, corresponding to only a fraction of monolayers (~15%).

4. Conclusions

A novel conjugated electroactive thiol derivative, 4-ferrocene thiophenol, was employed as capping agent to produce electroactive gold nanoparticles. Well-isolated nanoparticles were observed by TEM and the average core diameter was calculated as $\sim 2.5 \text{ nm}$, which corresponded to $\text{Au}_{490}\text{Fc}_{80}$. The formal potential of the electroactive gold nanoparticles was compared with that of $\text{C}_8\text{SH}/\text{C}_8\text{Fc}$ mixed MPCs and the positive shift was attributed to the solvation environment alternation. The surface coverage of the gold nanoparticles was calculated as only a small fraction (15%) of full MPC monolayers.

Acknowledgements

This work was financially supported by the Outstanding Youth Fund (No. 20125513) from the National Natural Science Foundation of China, the 100 People Plan from Chinese Academy of Sciences and the 100 Chinese Outstanding Ph D Fund.

References

- [1] A. Kumar, G.M. Whitesides, *Science* 263 (1994) 60–62.
- [2] K.S. Weber, S.E. Creager, *J. Electroanal. Chem.* 485 (1998) 17–22.
- [3] S.J. Green, J.J. Stokes, M.J. Hosteler, J. Pietron, R.W. Murray, *J. Phys. Chem. B* 101 (1997) 2663–2668.

- [4] M.J. Hostetler, J.E. Wingate, C.J. Zhong, J.E. Harries, R.W. Vachet, M.R. Clark, J.D. Londono, S.J. Green, J.J. Stokes, G.D. Wignall, G.L. Glish, M.D. Porter, N.D. Evans, R.W. Murray, *Langmuir* 14 (1998) 17–30.
- [5] S.W. Chen, R.W. Murray, *Langmuir* 15 (1999) 682–689.
- [6] M. Brust, M. Walker, D. Bethell, D.J. Schiffrin, R. Whyman, *J. Chem. Soc., Chem. Commun.* (1994) 801–802.
- [7] R.L. Whetten, J.T. Khoury, M.M. Alvarez, S. Murthy, I. Vezmar, Z.L. Wang, P.W. Stephens, C.L. Cleveland, W.D. Luedtke, U. Landman, *Adv. Mater.* 8 (1996) 428–433.
- [8] T. Kondo, M. Takechi, Y. Sato, K. Uosaki, *J. Electrochem. Soc.* 381 (1995) 203–207.