

# Nanostructured gold colloid electrode based on in situ functionalized self-assembled monolayers on gold electrode

Liang Wang <sup>a,\*</sup>, Junyue Bai <sup>a,b</sup>, Pengfei Huang <sup>a,b</sup>, Hongjing Wang <sup>a</sup>,  
Liyang Zhang <sup>a</sup>, Yuqing Zhao <sup>a</sup>

<sup>a</sup> College of Life Science, Dalian Nationalities University, Dalian 116600, PR China

<sup>b</sup> School of Environmental and Biological Science and Technology, Dalian University of Technology, Dalian, Liaoning 116024, PR China

Received 15 July 2006; received in revised form 5 August 2006; accepted 8 August 2006

Available online 8 September 2006

## Abstract

A novel method for fabricating nanostructured gold colloid electrode based on in situ functionalization of self-assembled monolayers (SAMs) of 4-aminothiophenol (4-ATP) on gold electrode is proposed. The in situ functionalization of 4-ATP SAMs yields a redox active monolayer of 4'-mercapto-*N*-phenylquinone diimine (NPQD). When the amino-rich surface is exposed to gold colloid, the citrate-stabilized gold nanoparticles (GNPs) can be anchored onto the surface of the in situ functionalized electrode by the electrostatic interactions and a new nanostructured gold colloid surface was obtained. The mixed monolayers of in situ functionalized product, NPQD, and 1,4-benzenedimethanethiol (BDMT) can provide a more compact and order platform to fabricate GNPs on the electrode surface. The film formed by this technique has the advantages of high organization and uniformity, which could provide a desirable microenvironment to assemble GNPs and facilitate the concentration of the analyte from the bulk solution to the electrode surface. The nanostructured gold colloid electrode has favorable effect on the electrochemical oxidation of naphthol isomers.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** 4-Aminothiophenol; In situ functionalization; 1,4-Benzenedimethanethiol; Gold nanoparticle; Mixed monolayers

## 1. Introduction

Organized, self-assembled monolayers (SAMs) on various solid supports have received intensive attention in recent years because they offer the possibility to control the film structure at the molecular and supramolecular level, thus enabling the tailoring of the surface properties [1]. Alkanethiols adsorbed on Au are the most studied SAMs systems because of their stability and high degree of organization. The SAMs of aromatic thiols have been used in the recent years to modify the coinage metal surfaces for a variety of applications [2–4]. Aromatic thiols are interesting for several reasons: the molecules are highly

anisotropic, and the intermolecular interactions are expected to be stronger than those between the alkanethiols, which may lead to different molecular packing structure. Moreover, higher electrical conductance would be expected in the aromatic thiol, as the electrons are delocalized in the benzene ring [5,6]. 4-Aminothiophenol (4-ATP) SAMs is an example of functional monolayers of aromatic thiols that can carry out certain functions due to the presence of some specific chemical group at the SAMs/electrolyte interface.

An area that has recently attracted much interest is the electrochemical polymerization of SAMs to yield two-dimensional polymer films covalently attached to a surface. In general, the monomer precursor is tethered to the surface via an alkyl chain, and the SAMs consisting of the monomer is polymerized electrochemically [2]. Lukkari and Ohsaka have, respectively, reported that

\* Corresponding author. Tel./fax: +86 411 87615619.

E-mail address: [wangliang101@hotmail.com](mailto:wangliang101@hotmail.com) (L. Wang).

surface-bound 4-ATP can be electrochemically oxidized to produce a new surface which exhibits reversible redox properties and they suggested that the oxidation leads to the formation of 4'-mercapto-*N*-phenylquin-one diimine (NPQD), the reaction mechanism follows head-to-tail coupling in neutral solution as in the case of acidic solution [1,6].

Herein a novel fabrication procedure for nanostructured gold colloid electrode based on in situ functionalization of 4-ATP SAMs on gold electrode was investigated. Gold nanoparticles (GNPs) have been extensively studied in electrochemistry for its special physico-chemical characteristics [7–14]. The use of GNPs nanostructures for the creation of electrochemical devices is an extremely promising prospect. The nanostructures give rise to porous, high-surface-area electrodes, where the local microenvironment can be controlled by the crosslinking elements and may lead to specific and selective interactions with substrates [15]. Various methodologies have been used for the tailoring of GNPs on electrode surfaces, which include the anchoring by electrostatic interaction, covalent linkage, electrochemical deposition, etc. [10,16–21]. Electrostatic assembly utilizes the negatively charged citrate surface of the particles, while covalent attachment relies on the reaction of the Au surface with thiols or disulfides to form Au<sup>0</sup>–S bonds [15].

The in situ functionalization of 4-ATP SAMs on gold electrode at physiological pH yields redox active monolayers of NPQD. When the amino-rich surfaces are exposed to gold colloid, the citrate-stabilized GNPs can be anchored onto the surface of the in situ functionalized electrode by the electrostatic interactions. The mixed monolayers of in situ functionalized product, NPQD, and 1,4-benzenedimethanethiol (BDMT) can provide a more compact and order platform to fabricate GNPs on the electrode surface and a new nanostructured gold colloid surface was obtained. The nanostructured gold colloid electrode can facilitate the concentration of the analyte from the bulk solution to the electrode surface and has favorable effect on the electrochemical oxidation of naphthol isomers.

## 2. Experimental

### 2.1. Chemicals and instrumentation

4-Aminothiophenol (4-ATP) and 1,4-benzenedimethanethiol (BDMT) were purchased from Sigma and they were used as received.  $\alpha$ - and  $\beta$ -Naphthol were purchased from Shanghai Chemical Company (China, Shanghai). All other chemicals were of analytical grade and were used without further purification. A 0.1 M phosphate buffer solution (PBS) was used to control the pH. All solutions were prepared with deionized water treated in a Millipore water purification system (Millipore Corp.). All experiments were carried out at room temperature.

Voltammetric measurements were performed with a CHI 440 electrochemical analyzer (CH Instruments,

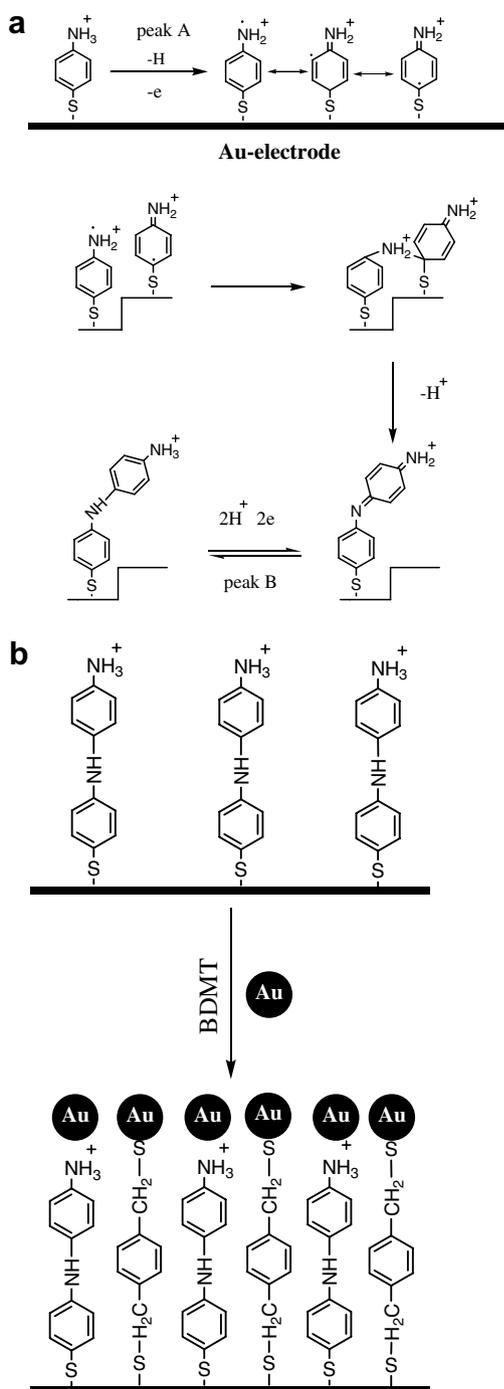
Chenhua Co. Shanghai, China). A conventional three-electrode cell was used, including a saturated calomel electrode (SCE) as reference electrode, a platinum wire counter electrode and a bare or modified gold working electrode. The pH values were measured with a PB-10 pH meter (Satorius). Unless otherwise stated, the electrolyte solutions were thoroughly degassed with N<sub>2</sub> and kept under a N<sub>2</sub> blanket.

### 2.2. Preparation of Au colloids

The 2.6 nm diameter colloidal Au was prepared according to the literature [22]. Typically, One milliliter of 1% HAuCl<sub>4</sub> was added to 90 ml of water at room temperature (20–23 °C). After 1 min of stirring, 2 ml of 38.8 mM sodium citrate was added. One minute later, 1 ml of freshly prepared 0.075% NaHB<sub>4</sub> in 38.8 mM sodium citrate was added and the colloidal solution was stirred for another 5 min and stored in a dark bottle at 4 °C.

### 2.3. Immobilization of Au colloidal particles by self-assembled technology

The working electrode was a Au disk electrode with a diameter of 2 mm. Prior to each measurement, the electrode was polished with diamond pastes and an alumina slurry down to 0.05  $\mu$ m on a polishing cloth (Buehler, Lake Bluff, IL), followed by sonicating in water and ethanol. Then, the Au electrode was electrochemically cleaned by cycling the electrode potential between 1.6 and –0.4 V (*vs.* SCE) in 0.5 M H<sub>2</sub>SO<sub>4</sub> until the cyclic voltammogram characteristic for a clean Au electrode was obtained. The SAMs of 4-ATP was fabricated by immersing the clean Au electrode into an ethanol solution of 10 mM 4-ATP for 1 h. The in situ functionalization of 4-ATP SAMs was carried out in 0.1 M PBS (pH 7.2) by cycling the potential between –0.2 and 0.7 V for several times and it was characterized by electrochemical measurement [6]. The resulting electrode is defined as NPQD/Au electrode. The NPQD/Au electrode was washed with PBS and kept in 0.1 M PBS (pH 7.2). The mixed monolayers were fabricated by immersing the NPQD/Au electrode into an ethanol solution of 10 mM BDMT for 1 h. The resulting electrodes will be referred as NPQD–BDM/Au electrode. The NPQD/Au electrode and NPQD–BDMT/Au electrode were subsequently soaked in the Au colloidal solution for 12 h at 4 °C, respectively. The resulting electrode was washed with copious amount of water and subjected to electrochemical experiments. Hereafter the nanostructured gold colloid electrodes will be referred as the GNPs/NPQD/Au electrode and GNPs/NPQD–BDMT/Au electrode, respectively. The process of in situ functionalization of 4-ATP SAMs is shown as A in Scheme 1 and the process of fabrication of nanostructured gold colloid electrodes is shown as B in Scheme 1.



Scheme 1. Schematic representation of the in situ functionalization of 4-ATP SAMs on gold electrode (a) and the fabrication of the nanostructured gold colloid electrode (b).

### 3. Results and discussion

#### 3.1. The absorption spectrum of colloidal Au

Fig. 1 depicts the absorption spectrum of colloidal Au. It has been shown that Au nanoparticles of diameter 2.6 nm would give an absorption maximum at around 514 nm whereas the particles of diameter 20–40 nm would

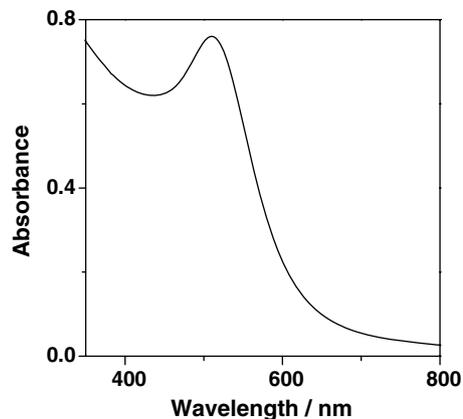


Fig. 1. Optical spectra of citrate stabilized colloidal Au.

exhibit an absorption band between 530 and 540 nm [23]. The Au nanoparticles of diameter 64 nm would give an absorption band at around 545 nm whereas the 120 nm particles would exhibit an absorption band at 620 nm [23]. As the absorption band of our nanoparticles shows absorption maximum at around 514 nm, it is considered that the nanoparticles would have a diameter around 2.6 nm. The aggregated nanoparticles are expected to give broad absorption band at around 700 nm [24]. In the present investigation, because the optical spectra obtained for the nanoparticles shows only one absorption band it is considered that the nanoparticles are not aggregated.

#### 3.2. In situ functionalization of 4-ATP SAMs

Fig. 2 shows the cyclic voltammograms (CV) obtained during the in situ functionalization of 4-ATP SAMs in 0.1 M PBS (pH 7.2). As shown in Fig. 2, the initial irreversible oxidative wave (peak A) at about 0.48 V at the first cycle is attributed to the electrochemical oxidation of the amine group in 4-ATP molecule at the electrode surface. In addition, a pair of reversible surface-confined redox couples at approximately 0.19 and 0.16 V (peaks B and B1) are assigned to the in situ formed surface-confined redox active

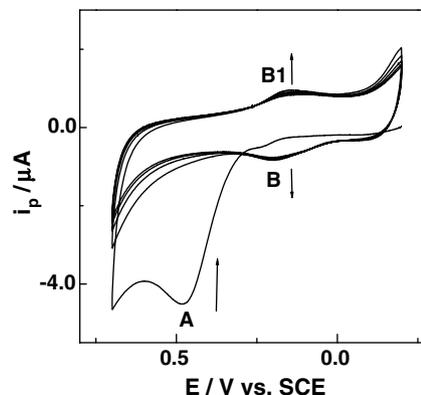


Fig. 2. Cyclic voltammograms of the in situ functionalization of 4-ATP/Au electrode in 0.1 M PBS (pH 7.2). Scan rate,  $100 \text{ mV s}^{-1}$ .

species, 4'-mercapto-*N*-phenylquinonediimine and 4'-mercapto-4-amin-odiphenylamine [1,2,25]. The redox peak corresponding to the aniline dimmer shifts by  $-56$  mV while increasing the solution pH by 1 unit, suggesting that protons and electrons take part in the redox reaction in the ratio of 1 to 1. According to literatures [1,25], the mechanism of the in situ functionalization of 4-ATP SAMs can be described as A in Scheme 1.

### 3.3. Characterization of nanostructured gold colloid electrode with cyclic voltammetry

Cyclic voltammetry of electroactive species  $\text{Fe}(\text{CN})_6^{3-/4-}$  is a valuable tool for testing the kinetic of the barrier of the interface. The extent of kinetic hindrance to the electron-transfer process increases with the increasing thickness and the decreasing defect density of the barrier. It has also been reported that the blocked heterogeneous electron transfer by the SAMs could be restored by assembling the GNPs onto the SAMs and the reversibility of redox couples (e.g.,  $\text{Fe}(\text{CN})_6^{3-/4-}$ ) at the nanostructured gold colloid electrodes varies with surface coverage of the GNPs and, in return, the reversibility of the electrode reaction could be used to probe the surface coverage of the GNPs [26,27].

Fig. 3 shows the CV responses of  $1.0$  mM  $\text{Fe}(\text{CN})_6^{3-/4-}$  at bare Au electrode, NPQD/Au electrode, GNPs/NPQD/Au electrode and GNPs/NPQD-BDMT/Au electrode, respectively. As can be seen,  $\text{Fe}(\text{CN})_6^{3-/4-}$  shows a couple of well-defined redox waves at bare Au electrode (Fig. 3, curve c) with a peak-to-peak separation ( $\Delta E_p$ ) of  $60$  mV at  $100$  mV s $^{-1}$ . After the Au electrode was in situ functionalized, a obvious decrease in redox peak current and increase in peak-to-peak separation ( $\Delta E_p = \sim 147$  mV) are observed (Fig. 3, curve a), indicating that the NPQD SAMs act as the inert electron and mass transfer blocking layer and thus hinders the diffusion of ferricyanide toward the electrode surface. On the other hand, when GNPs was

attached to the electrode surface, the voltammetric response of ferricyanide at the GNPs/NPQD/Au electrode is restored close to that obtained at the bare Au (Fig. 3 curve b), suggesting that the electron transfer process blocked with the SAMs of NPQD was clearly restored upon the GNPs layer onto the NPQD/Au electrode. This demonstrated that GNPs has been successfully assembled on Au surface and provide the necessary conduction pathways, besides acting like nanoscale electrodes in promoting the electron transfer between the analyte and the electrode surface. The redox peak current and peak-to-peak separation kept almost identical even the NPQD/Au electrode immersed in colloidal Au solution for a long time (more than 12 h) for the assembly of GNPs. This reflects that it is relatively difficult to achieve a higher coverage of the GNPs only by immersing the NPQD/Au electrode into colloidal Au solution. This is possibly due to the repulsive interaction between the surface-confined GNPs and free GNPs in solution [28,29].

In order to obtain a higher surface coverage of the GNPs onto the in situ functionalized electrode, the more compact pattern of mixed monolayers of NPQD and BDMT were utilized for anchoring GNPs. The reversibility of the  $\text{Fe}(\text{CN})_6^{3-/4-}$  couple at the GNPs/NPQD-BDMT/Au electrode ( $\Delta E_p = \sim 65$  mV) was dramatically improved even to about the same level as that at bare Au electrode and better than that at the GNPs/NPQD/Au electrode ( $\Delta E_p = \sim 80$  mV). The redox peak current of the  $\text{Fe}(\text{CN})_6^{3-/4-}$  couple at the GNPs/NPQD-BDMT/Au electrode was also dramatically improved even better than that at the bare Au electrode. These facts demonstrated that the mixed monolayers of NPQD and BDMT can provide a more compact and order platform to fabricate GNPs on the electrode surface. The prepared GNPs/NPQD-BDMT/Au electrodes were found to be relatively stable for voltammetric measurements. For example, the redox peak currents of the  $\text{Fe}(\text{CN})_6^{3-/4-}$  couple were found to be almost identical after continuously cycling the electrodes for 30 cycles.

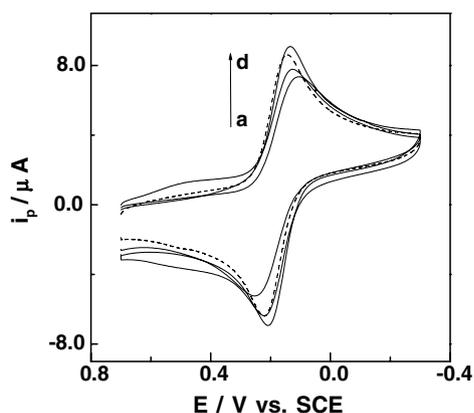


Fig. 3. Cyclic voltammograms of  $1.0$  mM  $\text{Fe}(\text{CN})_6^{3-/4-}$  at NPQD/Au electrode: (a), GNPs/NPQD/Au electrode (b), bare gold electrode (c), and GNPs/NPQD-BDMT/Au electrode (d), in  $0.1$  M KCl, respectively. Scan rate,  $100$  mV s $^{-1}$ .

### 3.4. Electrochemical oxidation of naphthol isomers at the nanostructured gold colloid electrode

In order to demonstrate that the nanostructured gold colloid electrode can facilitate the concentration of the analyte from the bulk solution to the electrode surface, the electrochemical oxidation of  $\alpha$ - and  $\beta$ -naphthol isomers at the nanostructured gold colloid electrode has been described.

Fig. 4 shows the cyclic voltammograms of the binary mixtures of  $\alpha$ - and  $\beta$ -naphthol (each  $0.1$  mM) in  $0.1$  M PBS (pH 7.2) at different electrodes. At the bare electrode, the electrochemical oxidation of  $\alpha$ - and  $\beta$ -naphthol occurs at approximately  $0.35$  and  $0.55$  mV, respectively (Fig. 4, curve a). The voltammetric peak is ill-defined, suggesting slow electron transfer kinetics. The GNPs/NPQD/Au electrode shows favorable effect on the electrochemical oxida-

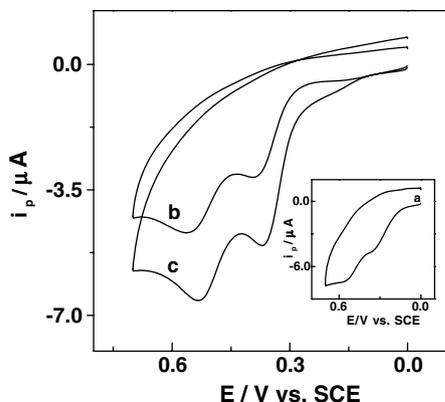


Fig. 4. Cyclic voltammograms for the binary mixtures of  $\alpha$ - and  $\beta$ -naphthol (each 0.1 mM) at bare gold electrode (a), GNPs/NPQD/Au electrode (b) and GNPs/NPQD-BDMT/Au electrode (c) in 0.1 M PBS (pH 7.2). Scan rate, 100 mV s<sup>-1</sup>.

tion of naphthol isomers.  $\alpha$ - and  $\beta$ -Naphthol yielded two well-defined oxidation peaks at the GNPs/NPQD/Au electrode. Meanwhile, the oxidation peak current also remarkably increased (Fig. 4, curve b). The reason for the better performance of the GNPs/NPQD/Au electrode in comparison with the bare electrode is probably connected with adsorption of analyte and product of reactions on large surface of the modified electrode which has three dimensional structure of nanostructured gold colloid. It is interesting to note that mixed monolayers fabricated gold colloid electrode, GNPs/NPQD-BDMT/Au electrode (Fig. 4, curve c), shows obviously more favorable effect on the electrochemical oxidation of naphthol isomers than that at the GNPs/NPQD/Au electrode. The reason for this is due to the higher surface coverage of the GNPs on the GNPs/NPQD-BDMT/Au electrode than that of the GNPs/NPQD/Au electrode.

#### 4. Conclusion

A novel nanostructured gold colloid electrode based on in situ 4-ATP SAMs on gold electrode was fabricated successfully. The mixed monolayers of in situ functionalized product, NPQD, and BDMT can provide a more compact and order platform to fabricate GNPs on the electrode surface and a new nanostructured gold colloid surface was obtained. The nanostructured gold colloid electrode shows favorable effect on the electrochemical oxidation of naphthol isomers. This demonstration may offer a new insight into interfacial electrochemistry of the metallic nanoparticles anchored onto the in situ functionalized conductive membrane and could provide a new platform for electrochemical investigations and electroanalytical

applications, such as for electrochemical investigation of isomers.

#### Acknowledgement

This project was supported by the Doctor Foundation of Dalian Nationalities University (20056101).

#### References

- [1] J. Lukkari, K. Kleemola, M. Meretoja, T. Ollonqvist, J. Kankare, *Langmuir* 14 (1998) 1705.
- [2] W.A. Hayes, C. Shannon, *Langmuir* 12 (1996) 3688.
- [3] C.R. Raj, A.I. Abdelrahman, T. Ohsaka, *Electrochem. Commun.* 7 (2005) 888.
- [4] L.S. Jiao, L. Niu, J. Shen, T.Y. You, S.J. Dong, A. Ivaska, *Electrochem. Commun.* 7 (2005) 219.
- [5] Q. Jin, J.A. Rodriguez, C.Z. Li, Y. Darici, N.J. Tao, *Surf. Sci.* 425 (1999) 101.
- [6] C.R. Raj, F. Kitamura, T. Ohsaka, *Langmuir* 17 (2001) 7378.
- [7] L. Zhang, X. Jiang, E.K. Wang, S.J. Dong, *Biosens. Bioelectron.* 21 (2005) 337.
- [8] L. Wang, E.K. Wang, *Electrochem. Commun.* 6 (2004) 49.
- [9] X.E. Jiang, L. Zhang, J.G. Jiang, X.H. Qu, E.K. Wang, S.J. Dong, *Chem. Phys. Chem.* 6 (2005) 1613.
- [10] A.R. Raj, T. Okajima, T. Ohsaka, *J. Electrochem. Chem.* 543 (2003) 127.
- [11] L. Wang, J.Y. Bai, P.F. Huang, H.J. Wang, L.Y. Zhang, Y.Q. Zhao, *Electrochem. Commun.* 8 (2006) 1035.
- [12] Y.Y. Sun, F. Yan, W.S. Yang, C.Q. Sun, *Biomater.* 27 (2006) 4042.
- [13] M. Tominaga, T. Shimazoe, M. Nagashima, I. Taniguchi, *Electrochem. Commun.* 7 (2005) 189.
- [14] W.W. Yang, J.X. Wang, S. Zhao, Y.Y. Sun, C.Q. Sun, *Electrochem. Commun.* 8 (2006) 665.
- [15] A.N. Shipway, M. Lahav, I. Willner, *Adv. Mater.* 12 (2000) 993.
- [16] J.S. Li, Z.S. Wu, H. Wang, G.L. Shen, R.Q. Yu, *Sensor. Actuat. B* 110 (2005) 327.
- [17] C.Y. Tsai, T.L. Chang, C.C. Chen, F.H. Ko, P.H. Chen, *Microelectron. Eng.* 78 (2005) 546.
- [18] Y. Li, G. Shi, *J. Phys. Chem. B* 109 (2005) 23787.
- [19] H. Li, Q.J. Wang, J.M. Xu, W. Zhang, L.T. Jin, *Sensor. Actuat. B* 87 (2002) 18.
- [20] Y.Z. Xian, H.T. Wang, Y.Y. Zhou, D.M. Pan, F. Liu, L.T. Jin, *Electrochem. Commun.* 6 (2004) 1270.
- [21] J.A. Harnisch, A.D. Pris, M.D. Porter, *J. Am. Chem. Soc.* 123 (2001) 5829.
- [22] K.R. Brown, D.G. Walter, M.J. Natan, *Chem. Mater.* 12 (2000) 306.
- [23] A. Doron, E. Katz, I. Willner, *Langmuir* 11 (1995) 1313.
- [24] K.C. Grabar, R.G. Freeman, M.B. Hommer, M.J. Natan, *Anal. Chem.* 67 (1995) 735.
- [25] L. Zhang, J.B. Jia, X.Q. Zou, S.J. Dong, *Electroanal.* 16 (2004) 1413.
- [26] K.R. Brown, L.A. Lyon, A.P. Fox, B.D. Reiss, M.J. Natan, *Chem. Mater.* 12 (2000) 314.
- [27] D. Bethell, M. Brust, D.J. Schiffrin, C. Kiely, *J. Electroanal. Chem.* 409 (1996) 137.
- [28] K.C. Grabar, P.C. Smith, M.D. Musick, J.A. Davis, D.G. Walter, M.A. Jackson, A.P. Guthrie, M.J. Natan, *J. Am. Chem. Soc.* 118 (1996) 1148.
- [29] L. Su, L.Q. Mao, *Talanta* 70 (2006) 68.