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Colloidal silver nanoparticles modified electrode and its application to the electroanalysis of Cytochrome *c*

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ABSTRACT

A colloidal silver nanoparticles (CSNs) chemically modified electrode was prepared and its application to the electroanalysis of Cytochrome *c* (Cyt. *c*) was studied. The CSNs were prepared by reduction of $AgNO_3$ with $NaBH_4$, and were stabilized by oleate. They could be efficiently immobilized on the surface of a silver electrode. The result showed that the CSNs could clearly enhance the electron transfer process between Cyt. *c* and the electrode compared with bulk silver electrode. Linear sweep voltammetric measurement of Cyt. *c* at the chemical modified electrode indicated that the oxidative peak current of Cyt. *c* was linear to its concentration ranging from 8.0 nmol L^{-1} to 3.0 μmol L^{-1} with the calculated detection limit was about 2.6 nmol L^{-1}. The direct electrochemistry of Cyt. *c* was also studied by cyclic voltammetry.

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1. Introduction

The study of nano-sized materials has attracted tremendous attention because of their potential use in microelectronics, catalysis, and chemical and biological sensors [1,2]. The high ratio of surface atoms with free valences to the cluster of total atoms gives rise to high catalytic activation, which has been used in electrochemical catalytic reactions [3]. Many nanoparticles have been widely used in constructing electrochemical biosensors, such as gold [4,5] Si [6] and SiO_2 nanoparticles [7,8]. Although those nanoparticles have been proven to be successful for preparation of biosensors, to explore other nanoparticles, which have good stability and are easy to synthesize, is still a challenge. Colloidal silver nanoparticles (CSNs), which are easy to synthesize, have attracted our attention due to their quantum characteristics of small granule diameter and large specific surface area as well as their ability to quickly transfer photoinduced electrons at the surfaces of colloidal particles [9–11]. Delfino et al. have prepared a hydrogen peroxide sensor based on horseradish peroxidase immobilized on a silver nanoparticles/cysteamine/gold electrode [12], and they also reported the giant enhancement of Raman signal near silver colloidal nanoparticles is exploiter to study the roman spectrum of yeast Cyt. *c* [13]. Sibbald et al. [14] studied reduction properties of Cyt. *c* on iodide modified silver nanoparticles.

Heme proteins are important in living cells, which contain the porphyrin complex of iron (II)–hemein or iron (III)–hemein as a prosthetic group. These proteins perform different physiological functions in the biological system [15]. Electrochemical studies of these proteins have attracted considerable attention [16,17], since fundamental studies of these proteins can provide, insight into physiological electron transfer processes as well as impetus for the further development of amperometric biosensors and bioelectrocatalytic systems [18]. Horse heart Cyt. *c*, a relatively simple metalloprotein, is an ideal model for studying biological electron transfer processes [19]. Unfortunately, it is difficulty for Cyt. *c* to undergo a facile redox process at conventional electrodes for the following reasons. Firstly, its electroactive center is deeply buried in electrochemically “insulated” peptide backbone; secondly, the protein would adsorb on the electrode surface, resulting in the denaturation and loss of both electrochemical and bioactivity. However, direct electrochemistry of redox proteins has great significance since it establishes a model for the mechanistic study of electron exchange among proteins in biological systems and provides a foundation for fabrication of the third-generation biosensors [20]. So many methods have been employed to realize the direct electrochemistry of the proteins [21–23].

Since silver is a good material for electrochemical studies of hemoprotein [24,25] and a good substrate electrode for the

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preparation of chemically modified electrodes. In this work, we fabricated colloidal silver nanoparticles modified silver electrode and studied its applications to the electroanalysis of Cyt. *c*. The experimental results demonstrated that the colloidal silver nanoparticles could clearly promote the electron transfer process between Cyt. *c* and the electrode. The oxidation peak current of Cyt. *c* was linear to its concentration ranging from 8.0 nmol L^{-1} to 3.0 μmol L^{-1}. The detection limit was about 2.6 nmol L^{-1}. The direct electrochemistry of Cyt. *c* was also studied by cyclic voltammetry.

2. Experimental

2.1. Reagents

Horse heart Cyt. *c* and bovine serum album (BSA) were purchased from Sigma Chemical Company and used without further purification. $NaBH_4$ was obtained from Fluka. All the other reagents were analytical grade or above. Pure water was used throughout, which was obtained using a Millipore Q water purification apparatus. Its resistivity was over 18 MΩ cm.

2.2. Apparatus

Electrochemical measurements were performed on a CHI 650b electrochemical system (CHI company, USA), and all experiments were carried out using a three-electrode cell with a saturated calomel electrode (SCE, Model 232C, Jiangsu Electroanalytical Instruments Factory, China) was used as reference electrode and a platinum electrode (Model 213, Jiangsu Electroanalytical Instruments Factory, Jiangsu, China) as the counter electrode. The substrate silver electrode was a disk electrode with a diameter 400 μm (99.99%, Jiangsu Electroanalytical instruments works, Jiangsu). The atomic force microscopy (AFM) image was obtained using Nanoscope IIIa (Digitao Instruments, Inc., Santa Barbara. CA). The absorption spectra were recorded with a UV–vis 3010 Spectrophotometer (Tokyo, Japan).

2.3. Preparation of CSNs

All glassware used in the following procedures was cleaned in a bath of freshly prepared 3:1 HNO_3 + HCl, thoroughly washed with water, and dried prior to use. Stock Solutions were stored in dark bottles.

The CSNs were prepared according to the literature [26]. A solution of ice-cold 1.0 mmol L^{-1} $AgNO_3$ 10 mL was added dropwise into 30 mL freshly prepared 1.5 mmol L^{-1} $NaBH_4$, with vigorously stirring in an ice-bath, a clear yellow colloid formed almost immediately. Then the mixed solution was stirred for another 2 h. The color of the colloid stabilized by oleate was turned to be brownish yellow after purification by dialysis with semi-transparent film. Before use, it was stored below 4 °C. The color of the colloid did not change further during storage for months after the purification procedure.

2.4. Electrode modification procedures

The silver disk electrode was mechanically polished to a mirror-finish with 0.05 μm alumina, rinsed with doubly distilled deionized water, and cleaned in doubly-distilled deionized water to remove any trapped alumina by ultrasonic waves. Then the modified silver disk electrode was fabricated by dropping 6 μL silver colloidal solution onto the electrode surface. The modified electrode was dried in air.

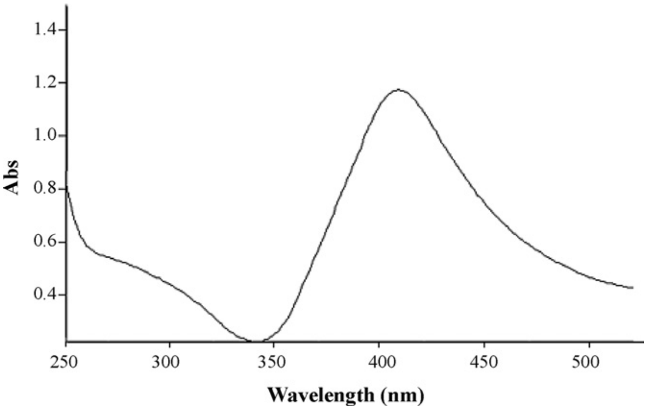

Fig. 1. UV–vis adsorption spectrum of the colloidal silver nanoparticles.

3. Results and discussion

3.1. Characteristic of colloidal Ag nanoparticles

Fig. 1 showed the characteristic UV–vis absorption of the hydrosol of oleate-capped silver nanoparticles. The band had a peak at 410 nm and a full width at the half-maximum of 75 nm, characteristic of rather monodispersed small silver particles [27], while uncapped silver colloid exhibited absorption with a maximum at 388 nm [28]. The shift of the absorption band provided clear evidence of the adsorption of oleate on the silver nanoparticles [29]. The good symmetric absorption peak implied that the size of the nanoparticles was very uniform. To detect the stability of the oleate-protected hydrosol of silver nanoparticles, we measured the absorption of the same hydrosol at different times. There was no obvious difference in the shape, position, and symmetry of the absorption peak during 40 days.

The nanoparticles were also examined by atomic force microscopy. Calculation demonstrated that they were spherical particles with average diameter of 15 nm.

3.2. Electrochemical behavior of the colloidal silver nanoparticles modified electrode

Fig. 2 showed the cyclic voltammograms of 0.07 mol L^{-1} HAc–0.13 mol L^{-1} NaAc buffer solution with pH 5.0 obtained at a silver electrode before (a) and after (b) it was modified with colloidal silver nanoparticles. At the bare silver electrode, there were no peaks between −0.5 V and +0.3 V on the CV curve, but the bold silver is oxidized when the potential was over +0.3 V. This is similar to the results reported by Chen and coworkers [24]. However, the CV curve obtained at the silver colloids modified silver electrode gave a pair of redox peaks at +0.242 V and +0.055 V vs. SCE, those were ascribed to Ag_{n-1}–Ag^+/Ag_n. Arnim and coworkers [30] was also reported that they are much more negative than that of the compact silver-metal electrode. And at a silver electrode the redox currents almost remain the same for 20 consecutive cycling. It means that colloidal silver nanoparticles can be efficiently immobilized on the silver electrode.

3.3. Direct electrochemistry of Cyt. c at the colloidal silver nanoparticles modified electrode

Fig. 3b showed the CV curve obtained at the CSNs modified electrode for 1.0 μmol L^{-1} Cyt. *c*. It gave a large couple of redox peaks, with the anodic and cathodic peak potentials at +0.220 V and −0.019 V vs. SCE, respectively. Furthermore, both of the redox peak currents increased when the more Cyt. *c* was added into the

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