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ScienceDirect
Electrochimica Acta 52 (2007) 8118–8124
ELECTROCHIMICA Acta
www.elsevier.com/locate/electacta

Electrocatalytic oxidation of ascorbic acid using a single layer of gold nanoparticles immobilized on 1,6-hexanedithiol modified gold electrode

A. Sivanesan, P. Kannan, S. Abraham John *

Department of Chemistry, Gandhigram Rural University, Gandhigram 624302, Dindigul, India

Received 30 April 2007; received in revised form 21 June 2007; accepted 10 July 2007
Available online 18 July 2007

Abstract

This paper describes the electrocatalytic oxidation of ascorbic acid (AA) in phosphate buffer solution by the immobilized citrate capped gold nanoparticles (AuNPs) on 1,6-hexanedithiol (HDT) modified Au electrode. X-ray photoelectron spectrum (XPS) of HDT suggests that it forms a monolayer on Au surface through one of the two −SH groups and the other −SH group is pointing away from the electrode surface. The free −SH groups of HDT were used to covalently attach colloidal AuNPs. The covalent attachment of AuNPs on HDT monolayer was confirmed from the observed characteristic carboxylate ion stretching modes of citrate attached with AuNPs in the infra-red reflection absorption spectrum (IRRAS) in addition to a higher reductive desorption charges obtained for AuNPs immobilized on HDT modified Au (Au/HDT/AuNPs) electrode in 0.1 M KOH when compared to HDT modified Au (Au/HDT) electrode. The electron transfer reaction of $[Fe(CN)_6]^{4-/3-}$ was markedly hindered at the HDT modified Au (Au/HDT) electrode while it was restored with a peak separation of 74 mV after the immobilization of AuNPs on Au/HDT (Au/HDT/AuNPs) electrode indicating a good electronic communication between the immobilized AuNPs and the underlying bulk Au electrode through a HDT monolayer. The Cottrell slope obtained from the potential-step chronoamperometric measurements for the reduction of ferricyanide at Au/HDT/AuNPs was higher than that of bare Au electrode indicating the increased effective surface area of AuNPs modified electrode. The Au/HDT/AuNPs electrode exhibits excellent electrocatalytic activity towards the oxidation of ascorbic acid (AA) by enhancing the oxidation peak current to more than two times with a 210 mV negative shift in the oxidation potential when compared to a bare Au electrode. The standard heterogeneous electron transfer rate constant (k_s) calculated for AA oxidation at Au/HDT/AuNPs electrode was 5.4×10^{-3} cm s^{-1}. The oxidation peak of AA at Au/HDT/AuNPs electrode was highly stable upon repeated potential cycling. Linear calibration plot was obtained for AA over the concentration range of 1–110 μM with a correlation coefficient of 0.9950. The detection limit of AA was found to be 1 μM. The common physiological interferents such as glucose, oxalate ions and urea do not show any interference within the detection limit of AA. The selectivity of the AuNPs modified electrode was illustrated by the determination of AA in the presence of uric acid.

Keywords: Gold nanoparticles; 1,6-Hexanedithiol; XPS; IRRAS; Cyclic voltammetry; Ascorbic acid; Uric acid

1. Introduction

Gold nanoparticles (AuNPs) are among the most extensively studied nano materials to date because of their unique size dependent physical, optical and electronic properties when compared to bulk gold [1–3]. Recently, modification of electrode surfaces with AuNPs has received much attention mainly due to their interesting electrocatalytic and biosensing applications [1–7]. Several strategies have been used to immobilize AuNPs on the electrode substrate which includes electrodeposition [5] and immobilization through covalent or electrostatic interactions with the self-assembled monolayers (SAMs) terminated with suitable functional groups [1,8–10]. Although AuNPs can be successfully immobilized on SAM modified electrodes but complete immobilization was not achieved on these surfaces due to inter-particle repulsion between the attached AuNPs and AuNPs in solution [11]. For example, it has been shown that only 10% coverage of AuNPs was achieved at the SAM terminated with amino functional group [10]. While higher surface coverage of AuNPs was attained only by preparing multilayer of

* Corresponding author. Tel.: +91 451 245 2371; fax: +91 451 245 3071.
E-mail address: abrajohn@yahoo.co.in (S. Abraham John).

0013-4686/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2007.07.020

AuNPs on the electrode substrate using layer by layer assembly method [9,12,13]. One way of assessing the surface coverage of AuNPs on the electrode substrate is the determination of electron transfer reaction of $[Fe(CN)_6]^{4-/3-}$ or $[Ru(NH_3)_6]^{2+/3+}$ in solution by cyclic voltammetry [9–13]. The electron transfer reaction of these redox species is very sensitive to the surface coverage of AuNPs on the electrode surface. As the surface coverage of AuNPs on the electrode substrate increases the electron transfer reaction of $[Fe(CN)_6]^{4-/3-}$ also increases [9–13].

Determination of ascorbic acid (AA) by voltammetric methods has received much attention in recent years [14]. It has been shown that the content of AA in biological fluids can be used to access the amount of oxidation stress in human metabolism and excessive oxidative stress has been linked to cancer, diabetes and hepatic disease [15]. It is known that accurate determination of AA using conventional electrodes is very difficult because of its high overpotential, poor reproducibility due to fouling effect caused by the oxidized products of AA, low selectivity and low sensitivity. Therefore, several approaches have been used to modify the electrode surfaces which includes ion-exchange polymers [16], various inorganic and organic materials [17,18] and SAMs terminated with different functional groups and [19–21]. In most of the cases, preconcentration is often needed before measurement and further these electrodes often show poor reproducibility.

Very recently, determination of AA using AuNPs attached on glassy carbon electrode (GC) modified with 4-aminobenzoic acid (ABA) followed by coupling with 4-aminothiophenol (ATP) [22] and multilayers of AuNPs/redox polymers have been reported [23]. The detection limit of 0.1 mM AA was reported at multilayers of AuNPs/redox polymers [23] while 2.8 μM was reported at AuNPs attached on GC modified electrode [22]. In the reported papers tedious procedures were adopted for the attachment of AuNPs on the electrode substrate [22,23]. For example, the multilayers of NPs/redox polymers were prepared on GC electrode by first electrodepositing osmium polymer on GC electrode, and then immersed in AuNPs solution followed by immersion in redox polymer solution and AuNPs solution, respectively for one more time [23]. In the other paper, first ABA was attached on GC electrode by potential cycling and then the ABA modified GC electrode was immersed in a mixture of ATP and coupling agent for 1 h and then immersed in AuNPs solution [22]. Herein we report a stable determination of AA with a detection limit of 1 μM using AuNPs modified electrode prepared by a very simple one step procedure. We have used 1,6-hexanedithiol (HDT) adsorbed on Au electrode for the attachment of AuNPs through covalent binding. In the present work, we have chosen −SH terminated thiol over $-NH_2$ terminated thiol for the immobilization of AuNPs because it is known that complete coverage of AuNPs on the SAM surfaces could not be achieved [10] and therefore it is expected that a possible electrostatic interaction between the positively charged amine and negatively charged ascorbate ions may enhance the oxidation of AA. However, such electrostatic interaction is absent when −SH terminated SAM was used. We found that AuNPs attached on HDT modified Au electrode enhanced the oxidation current of AA more than two times with 210 mV negative shift in the oxidation potential when compared to bare Au electrode. The application of the AuNPs modified electrode is further demonstrated by determining AA in the presence of uric acid.

2. Experimental

2.1. Chemicals

1,6-Hexanedithiol (Aldrich) and $HAuCl_4$ (Lancaster) were used as received. Sodium citrate, ascorbic acid and uric acid were purchased from Merck (India). Phosphate buffer solution (pH 7.2) was prepared by using Na_2HPO_4 and NaH_2PO_4. The Au working electrode was polished with alumina powder (0.5 μm) and sonicated in double distilled water for 5–10 min. The polished Au electrode was then electrochemically cleaned by cycling the potential between −0.2 and 1.5 V in 0.05 M H_2SO_4 at a scan rate of 10 V s^{-1} for 5 min or until the CV characteristics for a clean Au electrode were obtained.

2.2. Preparation of Au nanoparticles

Monodispersed colloidal Au nanoparticles were prepared by the reported procedure [24]. 75 mg of $HAuCl_4$ in 250 mL of distilled water (0.88 mM) was brought to a vigorous boil with stirring in a round-bottom flask fitted with a reflux condenser and then 26.25 mL of 1% sodium citrate (w/v) solution was rapidly added to the flask. The solution was boiled for another 15 min, during which the solution changed from pale yellow to deep red. The solution was allowed to cool to room temperature with continuous stirring and stored at 4 °C in a dark bottle until further use. The gold nanoparticles (AuNPs) prepared by this method were characterized by transmission electron microscopy and UV-Vis spectrophotometer. The TEM image and surface plasmon resonance band at 520 nm indicate that the average size of the AuNPs is 10–12 nm.

2.3. Modification of electrode surface

Immobilization of Au nanoparticles on polycrystalline Au electrode was carried out, as typically shown in Scheme 1. The monolayer of HDT was prepared on Au (Au/HDT) electrode by immersing a clean polycrystalline Au electrode into a 10 mM ethanolic solution of HDT for 3 h under nitrogen atmosphere. Then the Au/HDT electrode was subsequently washed with copious amount of ethanol and water to remove the loosely bound HDT molecules from the electrode surface and then dipped into Au colloidal solution for 12 h. The resultant electrode was washed with water and used for electrochemical measurements.

2.4. Instrumentation

Electrochemical measurements were performed in a conventional two-compartment three-electrode cell with a polished polycrystalline Au electrode (0.02 cm^2) as working electrode, a Pt wire as counter electrode and KCl saturated Ag/AgCl