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Size dependent electrocatalytic activity of gold nanoparticles immobilized onto three dimensional sol–gel network

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Abstract

The electrocatalytic activity of different sizes (2.6, 12.6, 20, 40 and 60 nm) of gold nanoparticles (AuNPs) immobilized onto (3-mercaptopropyl)-trimethoxysilane sol–gel modified Au electrodes (Au-MPTS) were examined by taking biologically important compounds such as ascorbic acid (AA), uric acid (UA) and 3,4-dihydroxyphenylacetic acid (DOPAC). The oxidation current of these compounds decreases and the oxidation potentials of them were shifted to more positive potential when the size of the immobilized AuNPs increases. Since AuNPs with smaller size provides higher surface area when compared to AuNPs with larger size, higher oxidation currents were observed for these compounds at smaller size AuNPs modified electrodes. AFM images show that AuNPs with 20 nm size were densely packed onto MPTS sol–gel film and generated continuous array whereas AuNPs with 60 nm size were less densely packed. The diffuse reflectance spectra (DRS) of 2.6 nm and 60 nm AuNPs immobilized onto MPTS sol–gel film show the absorption maximum around 520 nm and 540 nm, respectively indicating that the immobilized AuNPs were not aggregated in the sol–gel network. The AuNPs immobilized Au-MPTS electrodes successfully resolve the oxidation peaks of AA and UA in 0.2 M phosphate buffer solution (pH 7.2) whereas bare Au electrode fails to resolve the oxidation peaks of them. Interestingly the peak separation between AA and UA was identical (180 mV) irrespective of the size of AuNPs though the oxidation potentials of them were shifted to more positive potentials. Further, the detection limit of 200 nM DOPAC could be achieved at 2.6 nm AuNPs immobilized electrode whereas 500 nM was achieved at 60 nm AuNPs.

Keywords: Gold nanoparticles; Size dependent; Sol–gel electrode; Ascorbic acid; Uric acid; DOPAC

1. Introduction

Materials in nanosize exhibit unique physical and chemical properties because of their size, morphology and large surface area in contrast to bulk materials [1]. They have great potential applications in the fields such as catalysis [2,3], chemical, biochemical sensing [4–10] and biological imaging [7,11]. To date gold nanoparticles (AuNPs) have received much attention when compared to other metal nanoparticles mainly due to its ease in preparation, high stability and their shape and size dependent catalytic activity [6,12–17]. Several works have been reported in the literature on the catalytic effect of AuNPs with respect to their size [12–17]. However, only the electrocatalytic activity of AuNPs with respect to size was tested towards the reduction of H_2O_2 [18–21], O_2 [21] and oxidation of CO [22,23]. It has been reported that horseradish peroxide (HRP) labeled with AuNPs in smaller size greatly enhances the electrocatalytic reduction of H_2O_2 when compared to AuNPs in larger size [18–20]. Since AuNPs with small size help to immobilize more number of HRP on electrode surface due to its higher surface area show an enhanced electrocatalytic activity towards H_2O_2 [18–20]. The objective of the present study is to examine the electrocatalytic activity of AuNPs with respect to their size towards the oxidation of biologically important compounds such as ascorbic acid

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(AA), uric acid (UA) and 3,4-dihydroxyphenylacetic acid (DOPAC). It is known that the interesting characteristics of AuNPs would diminish when they gather to form larger clusters [2]. To retain its original properties the AuNPs should be immobilized in a dispersed state. For this purpose, we have chosen (3-mercaptopropyl)-trimethoxysilane sol–gel modified Au electrode (Au-MPTS) to immobilize 2.6, 12.6, 20, 40 and 60 nm sizes of AuNPs and tested the electrocatalytic activity of the immobilized AuNPs towards the oxidation of AA, UA and DOPAC. It was found that the oxidation peaks of these compounds were shifted to more positive potentials with decrease in the oxidation current when the size of the immobilized AuNPs increases. The sensitivity of AuNPs size towards the detection of DOPAC was studied using amperometric method. Detection limit of 200 nM was achieved for DOPAC at 2.6 nm immobilized AuNPs whereas only 500 nM was achieved at 60 nm AuNPs.

2. Experimental

2.1. Chemicals

$HAuCl_4 \cdot 3H_2O$, trisodium citrate and sodium borohydride were purchased from Aldrich and were used as received. (3-mercaptopropyl)-trimethoxysilane (MPTS) was purchased from Lancaster. All other chemicals used in this investigation were of analytical grade. Phosphate buffer (PB) solution (pH 7.2) was prepared by using Na_2HPO_4 and NaH_2PO_4.

2.2. Synthesis of different sizes of gold nanoparticles (AuNPs)

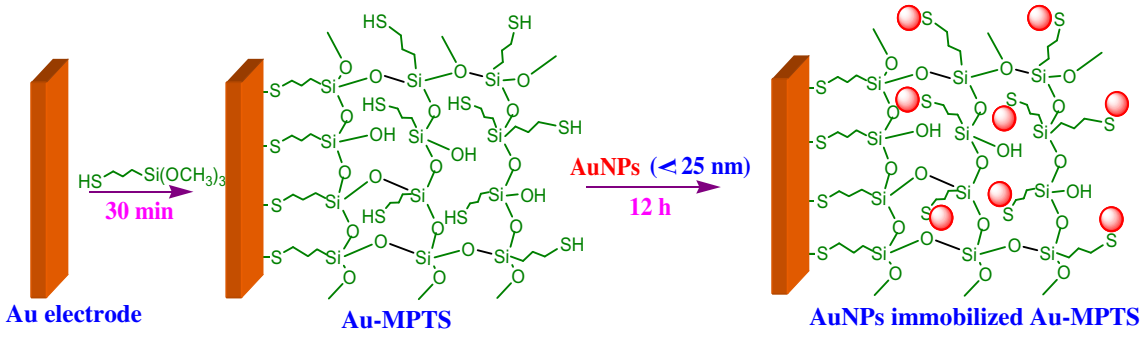
2.6 and 12.6 nm of AuNPs were prepared by the reported procedure [24]. AuNPs with 2.6 nm shows an absorption maximum at 514 while 12.6 nm shows absorption maximum at 518 nm in agreement with the previous report [24]. AuNPs with 20–60 nm size were synthesized by Frens method [25]. Colloidal solutions of 20, 40 and 60 nm AuNPs were prepared by adding 450, 330 and 230 μl of trisodium citrate in 50 ml of 0.01% $HAuCl_4$ solution, respectively. The synthesized AuNPs show absorption maximum at 523, 530 and 540 nm characteristic for 20, 40 and 60 nm of AuNPs, respectively.

2.3. Preparation of AuNPs immobilized sol–gel network on Au electrodes

The Au working electrodes were polished with 0.5 μm alumina slurry and sonicated in water for 15 min. The polished Au electrodes were 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 1 V s^{-1} for 10 min or until the CV characteristics for a clean Au electrode was obtained. (3-mercaptopropyl)-trimethoxysilane (MPTS) sol–gel was prepared by dissolving 0.1 M of MPTS in methanol/water/HCl mixture in the molar ratio of 1:3:3 and stirring the mixture vigorously for 30 min [26]. The cleaned Au electrode was immersed in MPTS sol–gel for 30 min at room temperature. The resulting sol–gel modified electrode was thoroughly washed with water to remove physically adsorbed silica sol. Then the electrode was immersed in a colloidal solution of AuNPs with different sizes for 12 h. The electrode was removed from the AuNPs solution after 12 h, washed with water and then used for electrochemical measurements. The covalent attachment of AuNPs with the sol–gel modified electrode is schematically shown in Scheme 1.

2.4. Instrumentation

Electrochemical measurements were performed in a conventional two-compartment three-electrode cell with a polished 1.6 mm Au as a working electrode, a Pt wire as counter electrode and a KCl saturated Ag/AgCl as reference electrode. All other electrochemical measurements were carried out with CHI model 650B (Austin, TX, USA) Electrochemical Workstation. AFM images were recorded by Digital Instruments Nanoscope IV, Veeco. The diffuse reflectance spectra (DRS) were recorded with HP8453 (RSA) spectrophotometer with an Agilent 8453 Labsphere-Reflectance accessory. Thin gold films produced by sputtering 99.99% pure gold on glass plates were used as substrates for AFM and DRS measurements. UV–Visible spectra were recorded with a Perkin–Elmer Lamda 35 Spectrophotometer.



Scheme 1. Schematic representation for the immobilization of AuNPs onto Au-MPTS electrode.