



Development of electrochemical sensors for the determination of selenium using gold nanoparticles modified electrodes

Rodrigo Segura^{a,*}, Jaime Pizarro^a, Karina Díaz^a, Alan Placencio^a, Fernando Godoy^a, Eduardo Pino^b, Francisco Recio^{c,d}

^a Departamento de Química de los Materiales, Facultad de Química y Biología, Universidad de Santiago de Chile (USACH), Santiago 33, Chile

^b Departamento de Ciencias del Ambiente, Facultad de Química y Biología, Universidad de Santiago de Chile (USACH), Santiago 33, Chile

^c Departamento de Química Inorgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Av. Vicuña Mackena 4860, Macul, Santiago de Chile, Chile

^d Centro de Nanotecnología y Materiales Avanzados, CIEN-UC, Pontificia Universidad Católica de Chile, Chile

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ABSTRACT

Electrochemical sensors have been developed for the determination of selenium (Se (IV)) using glassy carbon electrodes modified with gold nanoparticles (AuNPs) obtained electrochemically (GC/AuNPs/E) and chemically (GC/AuNPs/C) using square wave anodic stripping voltammetry (SWASV). GC/AuNPs/E was characterized by cyclic voltammetry (CV), atomic force microscopy (AFM), scanning electron microscopy (SEM), and X-ray dispersion spectrometry (EDS). The results indicate a homogeneous distribution of AuNPs with a 75 ± 20 nm particle size distribution. The chemically prepared AuNPs were characterized by transmission electron microscopy (TEM) and UV–vis spectroscopy (Surface Plasmon Band), and the results indicate that the AuNPs have a spherical shape (7.4 ± 1.3 nm). GC/AuNPs/C was prepared using a drop coating technique and was characterized by CV. The optimum conditions for the prepared electrodes were as follows: accumulation potential of -0.80 V (E_{acc}), accumulation time (t_{acc}) of 120 s, and a frequency of 15 Hz. A linear range was observed from 10 to $50 \mu\text{g L}^{-1}$ with a limit of detection (LOD) of $0.120 \mu\text{g L}^{-1}$ for GC/AuNPs/E, and a linear range was observed from 15 to $55 \mu\text{g L}^{-1}$ with a LOD of $0.175 \mu\text{g L}^{-1}$ for GC/AuNPs/C. The proposed procedure was validated with the TM-15 certified reference material, and good accuracy and precision were observed. In addition, this approach was applied to seawater samples with satisfactory results.

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1. Introduction

Selenium is an essential element for animals, plants, and humans. However, toxic effects have been observed in specific concentration ranges, and these effects can arise from an excess or deficiency of this metalloid. The World Health Organization (WHO) established the maximum limit of Se in drinking water to be $10 \mu\text{g L}^{-1}$ [1–3].

The determination of selenium in different matrices is very important in biochemical, environmental, and chemical analyses. Selenium can be determined by high performance liquid chromatography-inductively coupled plasma mass spectrometry (HPLC-ICP-MS) [4], hydride generator atomic absorption spectroscopy (HG-AAS) [5], graphite furnace atomic absorption

spectroscopy (GF-AAS) [6], gas chromatography (GC) [7], and various electroanalytical techniques (i.e., anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV), and adsorptive stripping voltammetry (AdSV)), which exhibit a high sensitivity and are inexpensive [8].

Electrochemical stripping techniques have been developed using mercury film electrodes (MFE) and hanging mercury drop electrodes (HMDE), which have high sensitivity and reproducibility. However, their use is restricted due to their high toxicity [9,10]. It is necessary to develop electrodes composed of environmentally friendly materials that have characteristics similar to those of the mercury electrodes. One novel alternative is the use of electrodes modified with nanomaterials, such as carbon nanotubes [11], graphene [12], and metal nanoparticles [13]. Due to their small size (1–100 nm), metal nanoparticles exhibit different physical, electronic and chemical properties compared to those of the bulk metals [14].

A solid gold electrode has been employed for the detection of arsenic [15], chromium [16], amino acids [17], and cadmium

* Corresponding author. Tel.: +56 227181172.

E-mail address: rodrigo.segura@usach.cl (R. Segura).

[18]. However, one approach of improving the sensitivity as well as the detection (LOD) and quantitation (LOQ) limits of the metals and metalloids is through the use of electrodes modified with AuNPs [19], which increase the effective surface area and mass transport to endow potential catalytic properties and excellent conductivity. These materials provide an alternative in the design and improvement of electrochemical sensors and biosensors [20].

The most common synthesis strategies for gold nanoparticles involve photochemical [21], electrochemical [22], or chemical reduction in the presence of a stabilizer (citrate or thiol) [23]. The electrodes modified with AuNPs have been used for the determination of different metals ions, such as Hg [24], Cu [25], As [26], Cr [27], Sb [28], Cd and Pb [29]. Mercury [30–33], gold [34] and silver [35] electrodes have been used with electrochemical techniques for selenium determination. However, the application of AuNPs for the determination of Se has not been previously reported.

In this study, a glassy carbon electrode modified with gold nanoparticles generated by electrochemical and chemical methods has been developed as an analytical methodology for the determination of selenium.

2. Experimental

2.1. Apparatus

The cyclic voltammetry and anodic stripping voltammetry experiments were carried out with a CH Instruments (USA) model 620C potentiostat. The three-electrode system consisted of a working glassy carbon electrode (CHI104, 3-mm diameter), a Ag/AgCl reference electrode (3 mol L⁻¹ KCl), and a platinum wire auxiliary electrode set up in a 10 mL electrochemical cell.

The GC/AuNPs/E surface was characterized by atomic force microscopy (AFM) (Nanoscope IIIa, Digital Instruments) in contact mode using silicon nitride (Si₃N₄) points. The modified electrodes were characterized by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) using a LEO 1420VP instrument with an acceleration voltage of 25 kV and a working distance of 11 mm.

Transmission electron microscopy (TEM) images were recorded on a JEM 2100 HT instrument. The UV–vis absorption spectrum was recorded on an Agilent 8453 instrument using a glass cell.

2.2. Reagents

All of the reagents were analytical grade. These reagents include tetrachloroauric acid (HAuCl₄ 99% Aldrich), trisodium citrate dihydrate (C₆H₅O₇Na₃·2H₂O, 98% Aldrich), sodium borohydride (NaBH₄ 96% Aldrich), a tetrachloroauric acid trihydrate standard solution (HAuCl₄·3H₂O, Merck), a perchloric acid solution (HClO₄, Mallinckrodt), and nitric acid solution (HNO₃, Merck) and a selenium standard solution (SeO₂ in HNO₃, 1000 mg L⁻¹, Merck).

2.3. Preparation of AuNPs

The chemical synthesis was performed according to a previously reported protocol [36]. 0.1 mol L⁻¹ NaBH₄ was added with stirring to an aqueous solution that contained 20 mL of 0.25 mmol L⁻¹ HAuCl₄ and 0.25 mmol L⁻¹ trisodium citrate. The AuNPs were characterized by TEM and UV–vis spectroscopy.

2.4. Preparation of electrodes

The glassy carbon electrodes were mechanically polished using 0.3 μm alumina with double-distilled water on a porous

surface. The electrodes were rinsed and sonicated for 15 min in double-distilled water. The three-electrode electrochemical cell was washed continuously with a 0.5 mol L⁻¹ HNO₃ solution.

2.4.1. GC/AuNPs/E:

In an electrochemical cell with 1.0 mL of 2.54 mmol L⁻¹ tetrachloroauric acid trihydrate and 9.0 mL of Milli Q water, an E_{acc} of -0.80 V, t_{acc} was applied for 60 s. The modified surface was characterized by SEM, AFM, and CV.

2.4.2. GC/AuNPs/C:

Using a drop coating technique, 20 μL of a colloidal suspension of the AuNPs was added to the surface of the electrode followed by drying at room temperature. To obtain a similar electroactive surface area on both types of electrodes, several drops of colloidal suspension were added to the electrode, and the optimal volume of AuNPs was determined to be 20 μL.

The surfaces of the modified electrodes were characterized by SEM, EDX, and AFM, and the electroactive surface areas were evaluated by cyclic voltammetry from 0.0 to 1.60 V using a scan rate of 0.1 V s⁻¹ in 1.0 mol L⁻¹ HClO₄. A final volume of 10 mL was achieved by adding MilliQ water (18 MΩ cm).

3. Results and discussion

3.1. Characterization of GC/AuNPs/E

The GC/AuNPs/E was characterized using AFM and SEM analyses. The AFM topographic image of GC/AuNPs/E (Fig. 1a) shows the homogeneous distribution of AuNPs, which had a cross section (Fig. 1b) with an average size of 75 nm and a roughness of 24.7 nm. The SEM analysis indicated a homogeneous distribution of AuNPs with an average size of 75.82 ± 20 nm, which is similar to the results obtained using AFM and EDX confirming the presence of gold on the electrode surface (Fig. 1c and d).

3.2. Characterization of GC/AuNPs/C

The chemically prepared gold nanoparticles were characterized by TEM and the surface Plasmon band (SPB). Fig. 2a shows the TEM image of the chemically prepared AuNPs, and the results indicate that spherical nanoparticles with an average diameter of 7.4 ± 1.3 nm were formed. This result is in good agreement with the SPB, which had a maximum absorption wavelength at 517 nm (Fig. 2b) and is in agreement with the literature results for spherical nanoparticles with a diameter of less than 9 nm [37,38].

Due to the small size of the AuNPs and their good distribution on the electrode, no relevant images were obtained by SEM and EDX.

3.3. Electrochemical characterization of GC/AuNPs/E and GC/AuNPs/C

Fig. 3 shows the voltammograms of the gold (Au), GC/AuNPs/E and GC/AuNPs/C electrodes at 0.1 V s⁻¹. The modified electrodes with AuNPs contain two anodic peaks at 0.93 and 1.12 V while the Au electrode at 1.24 and 1.46 V, which are associated with the formation of gold oxides. The cathodic peak was shifted to more negative potentials with the decrease in size of nanoparticles from 0.80 V (Au) to 0.70 V (GC/AuNP/E) and 0.68 V GC/AuNPs/C corresponded to the reduction of the formed gold oxides [39–42]. On the other hand, the oxygen evolution starts at less positive potentials to the electrodes containing AuNPs than gold electrode and the residual current was higher in the electrodes with

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