Electroanalysis of selenium in water on an electrodeposited gold-nanoparticle modified glassy carbon electrode

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A B S T R A C T

This work presents a simple and cheaper method of detecting selenium in water using an electrochemical sensor based on gold nanoparticle (AuNP) modified glassy carbon electrode. AuNPs were electrochemically deposited on a glassy carbon electrode (GCE) using cyclic voltammetry within the potential range of -0.4 mV to 1.1 mV for 10 cycles. The modification of GCE with AuNPs resulted in an increase in the electroactive surface area of the electrode which led to the enhancement of the redox current peaks of $[Fe (CN)_6]^{3-/4-}$ and $[Ru (NH_3)_6]^{2+/3+}$ in comparison to the bare GCE. Square wave anodic stripping voltammetry was used to detect Se (IV) in water (in 0.1 M H_2SO_4 as supporting electrolyte) at the following optimum conditions: pH 1, deposition potential of -100 mV, pre-concentration time of 60 s. The GCE-AuNP sensor was able to detect Se (IV) to the limit of 0.64 µg L^{-1} and was not susceptible to many interfering cations except Cu (II) and Cd (II). This method involves a simple one step electrode modification. The sensor was used to detect Se (IV) in a real sample. This method was validated by its good correlation with the result obtained from inductively coupled plasma method.

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1. Introduction

Selenium is a trace element that is important in our diet and in the health of plants and animals when taken in the correct amount [1]. Exposure to an excess amount of selenium is toxic and can cause health problems such as gastrointestinal upsets, hair loss, white blotchy nails, garlic breathe odour and nerve damage. Selenium deficiency on the other hand, has been linked to cancer, heart diseases, muscular dystrophy, multiple sclerosis, immune system, osteoarthopathy, reproductive disorder in humans and white muscle disease in animals [2]. The World Health Organization has set a limit of 10 µg L^{-1} selenium concentration in drinking water [3].

Human activities that have facilitated the increase in the concentration of selenium in the environment include the following: the mining and processing of base metal, gold and coal; phosphate deposits; the use of rock phosphate as fertiliser; the application of sewage sludge to land; the manufacture of detergents and shampoo; and so on. The increased use of selenium in the pharmaceutical, glazing, photocopying, ceramics, paint and electronics industries has also increased the amount of selenium entering the environment [4].

Owing to the toxicity and the environmental importance of selenium, its detection and quantification have been studied using various methodologies. The three main methods of selenium detection are inductively coupled plasma (ICP), spectroscopy and electrochemistry. Inductively coupled plasma has been used to detect selenium at low concentrations but the pitfall of this method is that it is expensive, it requires extensive sample preparation, it has a long analysis time and it requires sophisticated operator personnel [5]. The spectroscopic methods predominantly used are graphite furnace atomic absorption spectroscopy [6], hydride generation atomic absorption spectroscopy [7] and atomic fluorescence spectrometry [8].

Electrochemical techniques for selenium detection have an edge over the other techniques based on the grounds such as low cost of instrument, minimum sample preparation for analysis, faster analysis time and amenability to miniaturisation [9].

Bertolino et al. reported the speciation analysis of selenium in natural water using square wave voltammetry after pre-concentration on activated carbon and selenium was detected to a limit of 0.004 µg L^{-1} within 0.01 µg L^{-1}–20 µg L^{-1} concentration range [10]. In another report, Se (VI) was reduced to Se (IV) before analysis using flow injection anodic stripping voltammetry at a gold electrode for Se (IV) determination [11]. The Se (IV) concentration was calculated as the difference between the result for total inorganic selenium and Se (IV). The interfering divalent cations were removed by using cation exchange column prior to the injection value. Differential pulse adsorptive stripping voltammetry at a bismuth film electrode with cetyl trimethyl ammonium bromide and p-amino benzene sulphonic acid as a complexing agent, was used to determine trace selenium by Zhang et al. [12]. A detection limit of 0.1 µg L^{-1} and accumulation time of 300 s were used. Britta Lange et al. were able to determine Se (IV) by catalytic cathodic

stripping voltammetry in the presence of Rhodium. Rhodium was used for this work because of its catalytic ability. U.V. digestion was used to eliminate the interference caused by inorganic material and to convert Se (VI) to Se (IV) and a detection limit of 2.4 pM was obtained [13]. Attempts to use microelectrode in the determination of Se (IV) have also been reported [14]. Tan and Kounaves were able to determine Se (IV) at a micro fabricated Au ultra-micro electrode array using square wave anodic stripping voltammetry; they discovered that Se (IV) redox reaction appears to be kinetically faster and more reversible at the Au Ultra microelectrode (UME) array than at macro electrode or single Au UME. The limit of detection was 0.42 ppb [15].

In this work, gold nanoparticles were electrodeposited on glassy carbon electrode in a one step approach and used to detect Se (IV) by square wave anodic stripping voltammetry. The choice of supporting electrolyte, pH and deposition potential was optimised. The sensor was used to detect Se (IV) in both analytical and real water samples. The concentration of Se (IV) detected in real water sample was correlated with the result obtained from inductively coupled plasma optical emission spectrometry technique.

2. Experimental

2.1. Material and methods

$HAuCl_4$, KCl, Na_2SeO_3, HNO_3, KNO_3, K_2HPO_4, KH_2PO_4, NaOH, $K_3Fe(CN)_6$, $K_4Fe(CN)_6.3H_2O$, $Ru(NH_3)_6Cl_3$, $Ru(NH_3)_6Cl_2$, H_2SO_4 and KOH were purchased from sigma Aldrich. All chemicals were of highest analytical grade and deionised water was used for the preparation of solutions. All electrochemical measurements were done on Compactstat electrochemical workstation (Ivium Technologies, Netherlands), using a three-electrode configuration. The working electrode, counter electrode and reference electrode were glassy carbon electrode, platinum wire and Ag/AgCl (3 M KCl) respectively. The electrochemical cells were purged with ultra-pure argon gas for at least 10 min prior to all electrochemical measurements.

2.2. Electrode modification

Glassy carbon electrode (GCE) was modified with gold nanoparticles (AuNPs) according to the method reported by Arotiba et al. [16]. Briefly, GCE was modified with 5 mM of $HAuCl_4$ solutions by cycling the potential from −400 mV to 1100 mV for 10 cycles at a scan rate 50 mV s^{-1}, the reference electrode used is Ep vs Ag/AgCl (3 M KCl). The modified electrode was referred to as GCE-AuNPs. The modified electrodes were electrochemically characterised using square wave voltammetry and cyclic voltammetry (CV) in 5 mM mixture of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6.3H_2O$ (referred to as [Fe (CN) $_6$]$^{3-/4-}$) and 1 mM mixture of $Ru(NH_3)_6Cl_3$ and $Ru(NH_3)_6Cl_2$ (referred to as [Ru (NH$_3$)$_6$]$^{2+/3+}$) redox probes.

2.3. Selenium detection

Square wave anodic stripping voltammetry (SWASV) was used for the detection of selenium (IV) in 0.1 M H_2SO_4 on modified glassy carbon electrode. The pre-concentration potential and pre-concentration time were −100 mV and 100 s respectively. The SWVs were recorded at potentials ranging between 600 mV and 1000 mV to accommodate the stripping of selenium. The peak currents obtained from the SWASV of the various solutions were used to plot a calibration curve from which the regression equation was obtained. The electrode was subjected to a potential of 200 mV for 90 s to remove the excess selenium followed by a SWV sweep in Se (IV) free solution. Different concentrations of selenium were detected with a good detection limit. Furthermore, the GCE-AuNP electrode was used as a sensor for Se (IV) detection in tap water sample. For the purpose of validating the result obtained from this electrochemical sensor, inductively coupled plasma optical

emission spectrometry technique was also used to detect the amount of Se (IV) in the tap water sample.

3. Results and discussion

3.1. Electrode characterisation

Bare glassy carbon and GCE-AuNP electrodes were electrochemically characterised by using CV in [Fe (CN) $_6$]$^{3-/4-}$ and [Ru (NH$_3$)$_6$]$^{2+/3+}$ solutions; this was done by cycling a potential from −400 mV to 600 mV at a scan rate of 50 mV s^{-1}, to compare the peak current signal of the bare GCE and GCE-AuNPs. Fig. 1 shows the electrochemical responses of the bare and modified GCE in two common redox probes. As depicted in Fig. 1, the presence of AuNPs enhanced the interfacial electron transfer of Ferrocyannide and Ruthenium redox probes. This electrochemical enhancement is an indication of the potential application of GCE-AuNP electrodes in electroanalysis. The increase in current can be attributed to an increase in electroactive surface area of the electrode which can enhance the sensitivity of the electrode when used for electroanalysis [17].

3.2. Optimisation: the effect of supporting electrolyte, pH, deposition potential and deposition time

The effect of supporting electrolyte is presented in Fig. 2a. In this work, 0.1 M H_2SO_4 was chosen as the supporting electrolyte because it is more suitable for the stripping of Se (IV) due to the highest current signal obtained in comparison to other supporting electrolytes. The use of H_2SO_4 as a supporting electrolyte in the electrochemical detection of selenium has been reported [18]. The effect of pH on the availability of selenium for stripping was examined at pH of 1, 3, 6 and 10 as shown in (Fig. 2a). Such a study is important because the ionic states of metals can be affected by the proton environment (pH). An electrodeposition potential of −100 mV and electrodeposition time of 60 s were chosen as optimised parameters for the pre-concentration step. Claudete et al. were able to sense selenium by anodic stripping voltammetry using gold electrodes made from recordable CDs using deposition time of 60 s [18].

3.3. Electrochemical detection of Se

At the optimised conditions, GCE-AuNP electrodes gave a mark increased current response during the stripping of 10 ppm selenium (Fig. 3). This marked amplification of selenium signal is due to the fact that the electrodeposited gold has an affinity for selenium and they both interact to form an intermetallic compound Au–Se [19–20]. The
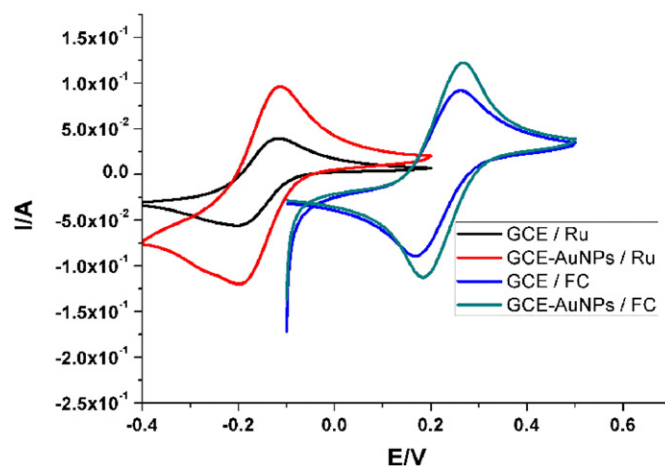

Fig. 1. An overlay of CVs recorded on bare GCE and GCE-AuNPs in 5 mM [Fe (CN) $_6$]$^{3-/4-}$ (labelled/FC) and in 1 mM [Ru (NH$_3$)$_6$]$^{2+/3+}$ (labelled/Ru) at 50 mV s^{-1} scan rate. E$_p$ vs Ag/AgCl (3 M KCl).