



Voltammetric detection of arsenic on a bismuth modified exfoliated graphite electrode



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ARTICLE INFO

Article history:

Received 15 June 2013

Received in revised form 20 August 2013

Accepted 21 August 2013

Available online 29 August 2013

Keywords:

Arsenic

Bismuth

Square wave anodic stripping voltammetry

Electrochemical sensor

Water

ABSTRACT

We present the application of a bismuth modified exfoliated graphite electrode in the detection of arsenic in water. Bismuth film was electrodeposited onto an exfoliated graphite (EG) electrode at a potential of -600 mV. The modification of EG resulted in an increase in the electroactive surface area of the electrode and consequently peak current enhancement in $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ redox probe. Square wave anodic stripping voltammetry was performed with the modified electrode (EG-Bi) in As (III) solutions at the optimum conditions of pH 6, deposition potential of -600 mV and pre-concentration time of 180 s. The EG-Bi was able to detect As (III) to the limit of $5 \mu\text{g L}^{-1}$ and was not susceptible to many interfering cations except Cu (II). The EG-Bi is low cost and easy to prepare.

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1. Introduction

Arsenic is a very toxic element that comes from both natural and anthropogenic sources. Human activities that contribute to arsenic pollution include wood preservatives, agricultural uses (such as pesticides and herbicides) and mining activity, burning coal and copper smelting. Industrial activities also contribute to arsenic pollution as a range of arsenicals are used in electro-photography, catalysts, pyrotechnics and antifouling [1–3]. The poisoning of water by arsenic has become a worldwide problem which has presented many challenges to scientists [4]. This is because long periods of exposure to As (III) concentrations higher than $10 \mu\text{g L}^{-1}$ can cause serious health problems such as skin lesions, peripheral neuropathy, diabetes, renal system effects, cardio-vascular diseases and cancer to human [3].

The environmental menaces caused by arsenic therefore necessitate various measures ranging from its detection to remediation. A wide variety of methods which include inductively coupled plasma and atomic absorption spectroscopy have been used for low level detection of As [5,6]. However, these techniques require expensive instrumentation, complicated procedures and are more suitable for laboratory conditions. Electrochemical techniques in the form of

sensors are also frequently used for the detection of As. Electrochemical sensors boast of low detection limits, rapid analysis times, low-cost instrumentation and on-site applicability [7–9]. They have been used for monitoring of an increasing range of toxic substances such as trace metals, carcinogens, organic pollutants (pesticide and phenols), explosives and nerve agents [8].

An electrochemical sensor can be made selective by a suitable choice of electrode potential and electrode material [10]. Some of the electrode materials commonly used include Pt, Au, C, Hg amalgams and semiconductors such as indium-tin oxide. The electrochemical application and performance of an electrode depends to a large extent on the material(s) from which it is made. Thus a number of factors such as electrical conductivity, chemical stability, surface reproducibility, mechanical properties, cost, availability and toxicity need to be considered in determining the suitability of an electrode [11].

Exfoliated graphite is a low density puffy material prepared from graphite (a low cost carbon material) and it has good electrical conductivity and high mechanical stability. This material can be easily fabricated into exfoliated graphite electrode by compression at high pressure [12]. Reports on the applications of EG electrodes in environmental, clinical or pharmaceutical fields are scarce. The first electrochemical studies on the EG electrode were reported by Frysz and Chung in 1997 [12]. They concluded that EG electrode offered better electron transfer rate, higher electrochemical area, and lower capacitance when compared to GCE [12]. To date, this promising electrode has not been well explored for myriads of

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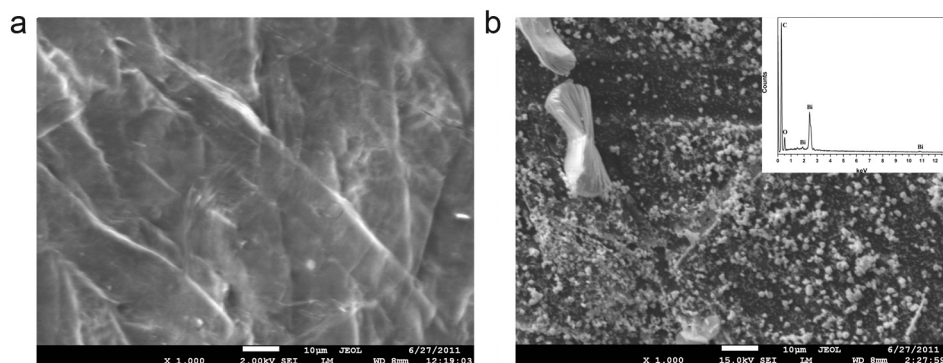


Fig. 1. (a) SEM micrograph of EG electrode. (b) SEM micrograph of EG-Bi electrode (inset: shows EDX spectrum of EG-Bi).

electrochemical analysis. This study, therefore, reports the possible uses of bismuth modified EG electrodes (EG-Bi) as an arsenic sensor in water.

2. Experimental

2.1. Material and methods

Natural graphite, BiO₂, KCl, As₂O₃, HNO₃, KNO₃, H₂SO₄ 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 an Autolab PGSTAT 302N using a three-electrode configuration. The working electrode, counter electrode and reference electrode were the Bi modified EG electrode, platinum wire and Ag/AgCl (3 M KCl) respectively.

2.2. Electrode modification

The EG material and electrode were prepared and fabricated as described earlier [13,14]. The electrodeposition of bismuth onto the EG (EG-Bi) was accomplished by using a previously reported method with a minor modification [15]. Briefly, bismuth oxide was electrodeposited by holding the potential at –600 mV for 300 s in 0.1 M HNO₃ supporting electrolyte containing 5 mM Bi₂O₃. The modified electrode was electrochemically characterised using cyclic voltammetry (CV) and square wave voltammetry (SWV) in a Ru(NH₃)₆^{2+/3+} redox probe.

2.3. Arsenic detection

Square wave anodic stripping voltammetry (SWASV) was used for the detection of arsenic. The EG-Bi electrode was used to record square wave voltammograms (SWV) of various concentrations of As (III) in 0.1 M KNO₃. This was done after a pre-concentration step at a potential of –600 mV for 180 s was carried out. The SWVs were recorded at potentials ranging between –500 mV to 300 mV to accommodate the stripping of As. 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 excess As followed by a SWV sweep in As (III) free solution.

3. Results and discussion

3.1. Electrode characterisation

The scanning electron micrograph in Fig. 1a and b confirms the presence of Bi nanoparticle after the electrodeposition step. These particles were identified as Bi from the energy dispersive

X-ray spectroscopy (Fig. 1b inset). The percentage of Bi on the electrode was reflected as 8.37%. The Bi particles had a spherical morphology and they were evenly distributed on the electrode surface displaying good electrode coverage. However, the ribbon-like micro-structures observed at some sites on the electrode surface (Fig. 1b) were as a result of agglomerations of the Bi nanoparticles.

The electrode was then electrochemically characterised using CV (not shown) and SWV in Ru(NH₃)₆^{2+/3+} redox probe and the results were compared to those obtained from the bare EG electrode. The modification of the EG electrode resulted in peak current enhancement compared to the bare EG electrode as illustrated by the SWVs shown in Fig. 2a. The increase in current was attributed to an increase in electroactive surface area of the electrode which can enhance the sensitivity of the electrode when used for electroanalysis. The electroactive surface area was calculated using the Randles–Sevcik equation (Eq. (1)):

$$i_p = 2.69 \times 10^5 n^{3/2} v^{1/2} D^{1/2} AC \quad (1)$$

where n is the number of electrons, v is the scan rate, A the area of the electrode, C is the concentration in mol L^{–1} and D is the diffusion coefficient of Ru(NH₃)₆^{2+/3+} in 0.1 M KCl which has been reported to be 8.8×10^{-6} cm² s^{–1} [16]. The electroactive area obtained by this method is related to the amount of electroactive sites for each electrode [17]. Electroactive surface areas of 13.1 mm² and 16.3 mm² were calculated for EG and EG-Bi electrode respectively. Thus the Bi nanoparticle enhanced the electroactive surface area by ca 24%. The EG-Bi electrode increased the interfacial kinetics rate of the redox probe as evident from lower peak potential separation (increased reversibility) when compared to EG electrode. The scan rate study (Fig. 2b) shows that this interfacial kinetics is also diffusion controlled because the peak current is proportional to the square root of scan rate. Diffusion controlled kinetics suggest that the concentration of an analyte can be deduced from the change in current of the system.

The modification of EG with Bi nanoparticle increased the conductivity of the electrode as seen in Bode plot (Fig. 2c) where EG-Bi has a lower impedance values at all frequencies measured than the bare EG. The modulus of impedance $|Z|$ on the y-axis of Bode plot is a measure of the total impedance of a system as shown in the equation $|Z| = \sqrt{(Z')^2 + (Z'')^2} = \sqrt{R^2 + (1/\omega C)^2}$ where Z' is the real impedance, Z'' is the imaginary impedance, R is impedance to the flow of charge, ω is the angular frequency and C is the capacitance. The main parameter of interest in highlighting the effect of electrode modification in our case is R . Thus lower impedance is expected if more charges or electrons are exchanged as observed in the EG-Bi electrode. Since smaller charge transfer resistance in Nyquist impedance plot translates to a lower $|Z|$ in the Bode plot, Fig. 2c also shows that the kinetics of electron transfer of the redox probe is faster at the EG-Bi interface.

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