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Fabrication of reduced graphene oxide-magnetic nanocomposite (rGO-Fe_3O_4) as an electrochemical sensor for trace determination of As(III) in water resources

Akajionu Benjamin Chimezie[a], Reza Hajian[a,*], Nor Azah Yusof[a,b], Pei Meng Woi[c], Nafiseh Shams[c]

[a] *Functional Devices Laboratory, Institute of Advanced Technology, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia*
[b] *Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia*
[c] *Department of Chemistry, Faculty of Science, University of Malaya, Kuala Lumpur 50603, Malaysia*

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ABSTRACT

In this work, an electrochemical sensor has been developed for trace determination of As(III) in water resources using differential pulse anodic stripping voltammetry (DPASV), on the surface of screen printed electrode modified reduced graphene oxide-magnetic nanocomposite (rGO-Fe_3O_4/SPE). Field Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM) showed a homogeneous distribution of Fe_3O_4 nanoparticles on GO sheets with an average size of 15.90 ± 0.84 nm. Raman spectroscopy and Electrochemical Impedance Spectroscopy (EIS) studies demonstrate that while As(III) was reduced to As^0, during deposition step (-0.5 V, 300 s), GO nanosheets were electrochemically reduced to rGO to provide more sensitive and conductive substrate. Under optimized conditions, the anodic peak current was proportional to the As(III) concentration over a wide range of 2–300 $\mu g\ L^{-1}$, with a detection limit and quantitative limit of 0.10 and 0.33 $\mu g\ L^{-1}$ (S/N = 3) respectively. The proposed As(III) electrochemical sensor also exhibited a relative standard deviation of 3.2% for six replicate analysis of 50 $\mu g\ L^{-1}$ As(III). Stability test showed the sensor retained ~93% of its initial signal after 30 successive measurements and ~90% of its initial measurement after two weeks storage at room temperature. In addition, the fabricated sensor was successfully employed for determining the As(III) residue in several water samples including lake water, reverse osmosis drink water and mineral water. The results were in agreement with inductively coupled plasma mass spectrometry (ICP-MS) when compared.

1. Introduction

Arsenic, a naturally occurring poisonous chemical element is recognized as one of the world's greatest environmental hazardous agents. Its presence in water resources has threatened human living as well as other organisms, and hence poses a serious environmental problem throughout the world [1]. In water resources, inorganic arsenic exits in two major chemical forms, arsenite (As(III)) and arsenate (As(V)). While As(V) is the major form, As(III) is more soluble in water and approximately 50 times more toxic than As(V) [2].

Various accurate analytical methods have been developed for trace As(III) detection, including Hydride Generation Atomic Fluorescence Spectroscopy (HG-AAS) [3], Graphite Furnace Atomic Absorption [4], Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [5], High-Performance Liquid Chromatography with either Chemical Vapour Generation (HPLC-CVG) [6] or Inductively Coupled Plasma Mass Spectrometry (HPLC-ICP-MS) [7]. However, these are traditional laboratory techniques, requiring the use of sophisticated instrumentation, complicated sample preparation processes, high operating cost and well-trained technician; hence they are not suitable for routine-in-field monitoring of a large number of samples.

In recent decades, development of electrochemical sensors, as convenient alternative methods, have been undergoing revolutionary changes, to achieve cost effective detection techniques with high sensitivity, lower detection limit, and short analysis time as well as simple and easy mode of operation. In this regard, electrochemical detection of As(III) has been achieved using mercury [8,9], platinum [10,11], and gold [12,13] among other solid electrodes, as well as their modified surfaces [14–17]. Through these, mercury and gold electrodes as well as gold modified surfaces provide higher sensitivity. However, electrochemical sensors fabricated using these electrodes have some operational limitations such as expensive nature of gold, toxicity of

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* Corresponding author.
E-mail address: rezahajian@upm.edu.my (R. Hajian).

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Mercury and the need to be operated in strong acidic medium which often leads to generation toxic arsine gas. Hence, there is need for fabrication of cheap and environmentally friendly electrochemical sensor, using readily available raw materials, for detection of As(III) in moderate conditions.

The recent use of nanomaterials, such as graphene as well as its derivatives and metal nanoparticles, as electrode modifiers in fabrication of electrochemical sensors, has led to improved sensitivity and lower detection limit, since these modifiers are able to mediate and catalyse detection mechanism. Based on this, electrochemical detection of trace As(III) using graphene-lead oxide nanocomposite based on exfoliated graphene oxide modified glassy carbon electrode (EGO/GCE) [18] and electro-reduced graphene oxide-gold nanoparticles nanocomposite film at glassy carbon electrode (ERGO-AuNPs/GCE) were reported as sensitive methods for detection of As(III) in HCl as supporting electrolytes [19]. Sequential injection/anodic stripping voltammetry, using long-lasting gold-modified screen-printed carbon electrode also have been developed for arsenic determination [20]. Also, graphene–platinum nanocomposite was reported as a sensitive and selective voltammetric sensor for trace level of arsenic quantification [21]. Yet, these reports are partly based on the use of expensive and toxic materials.

Iron-oxide (Fe_3O_4), a low-cost, environmentally friendly and easy to prepare nano-material has been reported to be very effective in removal of environmental contaminants including heavy metals ions such as arsenic (arsenate and arsenite ions), from water resources [1,22–25]. It emerges as a new class of nanoparticle due to its considerably high saturation magnetization, interesting electronic transport properties, low toxicity and high bio-compatibility [26]. In contrast, graphene, a planar, two-dimensional (2D) one atom thick nanomaterial, consisting of sp^2-hybridized carbon atom, has attracted great interest among scientists in various fields as well as sensor technology due to its unique properties such as high surface area, excellent thermal conductivity, high-speed electron mobility at room temperature, extraordinary electro-catalytic and optical properties [27–29]. Stripping analysis of As(III) has also been achieved by means of screen printed electrode modified with gold nanoparticles [30] and carbon black nanocomposites [31].

Recently, rGO/Fe_3O_4 nanocomposite has demonstrated to be a potential electrochemical and bio-electrochemical sensing platform for simultaneous detection of ascorbic acid, dopamine and uric acid as well as electro-catalytic determination of nitrite. In the fabrication method of nanocomposite, chemical reduction of GO to rGO and the in-situ formation of Fe_3O_4 nanoparticles on graphene sheet were accomplished in one-step reaction [32,33].

Generally, GO-metal nanocomposites are synthesized by hydrothermal and/or solvothermal in-situ reduction/co-precipitation of metal nanoparticles onto GO sheets [34,35]. However, this method lack in control of the size, loading ratio and distribution of the metal nanoparticles over GO, which limit their practical applications. In this regard, we presented a new voltammetric sensor based on ex-situ synthesis of Fe_3O_4 nanoparticles and its controlled assembly on GO sheets for the development of highly efficient GO-Fe_3O_4 nanocomposite electrochemical sensor for As(III) detection using differential pulse anodic stripping voltammetry (DPASV). It was shown that DPASV was able to reduce GO nanosheets in-situ during deposition step (− 0.5 V, 300 s) in sample solution.

2. Experimental

2.1. Reagents

Graphite powder (Asbury Graphite Mills Inc., USA), sulphuric acid (H_2SO_4, 98%), phosphoric acid (H_3PO_4, 85%, Merck, Germany), sodium nitrate ($NaNO_3$, 99.9%), hydrogen peroxide (H_2O_2,30%), potassium permanganate ($KMnO_4$, 99.9%), iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), iron(II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$), arsenic trioxide (As_2O_3), phosphate buffer solution, ammonia solution (NH_3, 30%) and all other chemicals were of analytical grades and used as received without further purifications. Milli-Q water (18 MΩ cm^{-1}) was used to prepare all aqueous solutions.

2.2. Instrumentation

All cyclic voltammetry (CV) and differential pulse voltammetric (DPV) measurements were performed using a computer controlled DropSens 8400 electrochemical system (Metrohm Co., Herisau, Switzerland) at room temperature. Electrochemical Impedance Spectroscopy (EIS) of the modified screen printed electrode (SPEs) were studied using VersaStat 3-300, Princeton, USA. The structural compositions and surface morphology of the synthesized GO, Fe_3O_4 and nanocomposites were characterized using Fourier transform infrared spectroscopy (FTIR, Perkin Elmer) and field emission scanning electron microscopy coupled with energy dispersive X-ray (FESEM-EDX, JEOL JSM 7600F). A digital pH meter (Fisher science education, Waltham, MA, USA) was used to adjust pH of solutions before each measurement. Kubota 2100 centrifuge (Tokyo, Japan) was used for centrifugation.

2.3. Fabrication of GO-Fe_3O_4/SPE

2.3.1. Synthesis of graphene oxide (GO)

Graphene oxide was synthesized from graphite flakes using improved Hummer's method with some modifications [36,37]. In order to oxidize graphite flakes, a mixture of sulphuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) in the ratio of 9:1 was added to a mixture of graphite (5 g) flakes and sodium nitrate (2.5 g) and stirred in an ice bath for 10 min. Then, $KMnO_4$ (15 g) was added slowly so that the temperature of the mixture remained below 5 °C while under continues stirring. The one-pot mixture was left for 3 days under stirring condition for proper oxidation of graphite. Colour change from dark purplish green to brown was an evidence that oxidation has occurred. To bring the reaction to the end, deionized water was added until the volume of the suspension was 400 mL. After 5 min, H_2O_2 (15 mL) was added to the solution (colour of the mixture changed to bright yellow). The reaction product was washed and centrifuged with 1 M HCl solution to achieve pH of 4.5. Finally a gel form of GO, which is due to exfoliation of the graphite oxide was prepared.

2.3.2. Synthesis of magnetic nanoparticles (Fe_3O_4)

Fe_3O_4 was prepared by co-precipitation of mixed solutions of $FeCl_3{\cdot}6H_2O$ and $FeCl_2{\cdot}4H_2O$. In brief, 1.0 mL of $FeCl_2{\cdot}4H_2O$ (2 M) and 4.0 mL of $FeCl_3{\cdot}6H_2O$ (1 M) were mixed in a 100 mL beaker and stirred with a magnetic stirring bar. Then 50 mL of 0.7 M aqueous NH_3 was added in dropwise. Magnetite, a black precipitate began to form throughout the slow addition of the ammonia solution over a period of 20 min. The magnetic nanoparticles (Fe_3O_4 NPs) was attracted to the bottom of the beaker using a strong magnet to decant the clear liquid and then rinsed up to 5 times with deionized water and dried in ambient temperature.

2.3.3. Fabrication of GO-Fe_3O_4/SPE

The nanocomposite (GO-Fe_3O_4) was prepared by liquid-self-assembly of the pre-formed Fe_3O_4 NPs on graphene oxide sheet. In brief, an amount of GO was exfoliated in water via sonication for 30 min to give 0.1 mg L^{-1} GO dispersion. 5 mL of 0.1 mg L^{-1} GO and 0.5 mL of 0.01 mg L^{-1} Fe_3O_4 solutions were mixed together into 20 mL beaker and further sonicated for 40 min at room temperature to obtain even distribution of Fe_3O_4 on GO sheet. 7 μL of the Fe_3O_4-GO suspension was drop casted on SPE working surface and allowed to dry overnight at ambient temperature.