



International Journal of Smart and Nano Materials

ISSN: 1947-5411 (Print) 1947-542X (Online) Journal homepage: <http://www.tandfonline.com/loi/tsnm20>

Graphene-platinum nanocomposite as a sensitive and selective voltammetric sensor for trace level arsenic quantification

R. Kempegowda, D. Antony & P. Malingappa

To cite this article: R. Kempegowda, D. Antony & P. Malingappa (2014) Graphene-platinum nanocomposite as a sensitive and selective voltammetric sensor for trace level arsenic quantification, International Journal of Smart and Nano Materials, 5:1, 17-32, DOI: [10.1080/19475411.2014.898710](https://doi.org/10.1080/19475411.2014.898710)

To link to this article: <http://dx.doi.org/10.1080/19475411.2014.898710>



© 2014 The Author(s). Published by Taylor & Francis.



Published online: 01 Apr 2014.



Submit your article to this journal [↗](#)



Article views: 1035



View related articles [↗](#)



View Crossmark data [↗](#)



Citing articles: 6 View citing articles [↗](#)

Graphene–platinum nanocomposite as a sensitive and selective voltammetric sensor for trace level arsenic quantification

R. Kempegowda^a, D. Antony^b and P. Malingappa^{a*}

^aDepartment of Chemistry, Bangalore University, Central College Campus, Bangalore 560001, India; ^bRaman Research Institute, C.V. Raman Avenue, Bangalore 560080, India

(Received 1 November 2013; final version received 23 February 2014)

A simple protocol for the chemical modification of graphene with platinum nanoparticles and its subsequent electroanalytical application toward sensitive and selective determination of arsenic has been described. Chemical modification was carried out by the simultaneous and sequential chemical reduction of graphene oxide and hexachloroplatinic acid in the presence of ethylene glycol as a mild reducing agent. The synthesized graphene–platinum nanocomposite (Gr–nPt) has been characterized through infrared spectroscopy, x-ray diffraction study, field emission scanning electron microscopy and cyclic voltammetry (CV) techniques. CV and square-wave anodic stripping voltammetry have been used to quantify arsenic. The proposed nanostructure showed linearity in the concentration range 10–100 nM with a detection limit of 1.1 nM. The proposed sensor has been successfully applied to measure trace levels of arsenic present in natural sample matrices like borewell water, polluted lake water, agricultural soil, tomato and spinach leaves.

Keywords: arsenic; graphene–platinum nanocomposite; chemical modification; square-wave anodic stripping voltammetry; spinach leaves

1. Introduction

The presence of heavy metal ions even at trace level in the environment has been considered as a major concern in recent years due to their toxicity and prolonged distribution [1]. Hence, quantification of these ions at trace level becomes a major area of research in the field of environmental science and technology. Arsenic is considered to be one of the naturally occurring highly toxic elements which are widely distributed in nature and cause serious threat to both mankind and aquatic systems even at ultra trace level [2]. Therefore, the World Health Organization (WHO) has recommended a maximum threshold limit value of 10 ppb for arsenic in drinking water [3]. Generally, arsenic exists in +3 and +5 oxidation states, former is approximately 60 times more toxic than the latter, and hence its concentration measurement is essentially required toward environmental concern [4]. Several methods have been employed for the determination of arsenic including spectroscopic methods like atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectroscopy (ICPAES) and UV-Vis spectroscopy. These

*Corresponding author. Email: mprangachem@gmail.com

Present address for R. Kempegowda: Department of Chemistry, Siddaganga Institute of Technology, Tumkur, Karnataka, India.

methods can be successfully applied in the determination of arsenic well below the guideline levels prescribed by WHO. However, these methods are time intensive and require high capital cost, skilled personnel to operate the instruments, prolonged sampling procedures and expensive day-to-day maintenance. In contrast, electrochemical methods offer comparably superior merits over these methods. The superiority of the electrochemical methods is due to their high sensitivity, field applicability and possibility of determining multiple analytes in single measurement [5]. Therefore, significant focus has been made in recent years to develop electrochemical sensors to quantify arsenic at trace level. In all these methods, chemical modification of working electrode toward the arsenic plays a key role in achieving the required selectivity, sensitivity and desired detection limit [6]. Modification of electrode surface using metal nanoparticles is one of the fascinating approaches in designing electrochemical interface for the electrocatalysis. The nanosized transition metal particles are of great interest due to their unique catalytic, electronic properties and noble performance over their bulk counterparts [7]. The catalytic properties of the metal nanoparticles are associated with the quantum scale dimensions and large surface-to-volume ratio, and availability of specific binding sites on the surface of the particles constitutes the driving force in the nanoparticle-based electroanalysis [8]. Gold, iridium oxide and cobalt oxide nanoparticles have been widely used in the determination of arsenic, whereas very few reports are available on the use of platinum [9–13]. Therefore, it is worthwhile to develop a sensing platform using platinum nanoparticles. It is generally accepted that the shape, size, surface structure of the nanoparticles and the catalyst support have tremendous influence on their catalytic properties [7]. Graphene-modified electrodes have been widely used as substrate material for wide variety of applications due to its fast electron transfer sites. In order to improve its analytical performance toward particular applications, they have been modified with nanoparticles. Various carbon-based supports have been used to anchor the nanoparticles, which include graphite, glassy carbon, carbon nanotubes and thin diamond films, among which graphene became a significant substrate material to anchor the metal nanoparticles due to the availability of large surface area to accommodate the nanoparticles. These nanoparticle-modified graphene composites were used as sensing and biosensing platforms [14–17]. In this report, we have made an attempt in designing chemically modified graphene sheets with platinum nanoparticles in the presence of ethylene glycol as a chemical reducing agent. The fabricated nanocomposite was used in the electrochemical determination of arsenic and subsequently applied to wide variety of environmental sample matrices using square-wave anodic stripping voltammetry (SWASV), with least interference from most of the common cations and anions.

2. Materials and methods

2.1. Apparatus

All electrochemical measurements were carried out using electrochemical analyzer (CH Instruments, 3700, Tenneson Hill Drive, Austin, TX, USA, Model: CHI 619B) at room temperature in an electrochemical cell of 10 mL volume with a standard three-electrode configuration. Graphene–platinum nanoparticle-modified glassy carbon electrode (GCE) (diameter = 5 mm) acted as the working electrode, a Pt (purity 99.99%) wire as the counter electrode and Ag/AgCl (3M KCl) as reference electrode (CH Instruments). Before electrochemical measurements, all the solutions were degassed using ultra pure nitrogen gas for about 15 minutes. SWASV was used in the potential range -0.2 to 0.8 V with an

amplitude of 0.025 V, frequency of 40 Hz and 0.004 V of potential increment. All pH measurements were carried out using Control Dynamics pH meter (Model: APX 175, Control Dynamics Instruments, Mumbai, India). Infrared spectrometric measurements were recorded using Fourier transform infrared spectroscopy (FTIR) Shimadzu spectrometer (Model: 8400S, Shimadzu Corporation, Kyoto, Japan) in the range 1000–4000 cm^{-1} with a resolution of 4 cm^{-1} . The surface morphology and particle size of platinum nanoparticle-decorated graphene sheets were characterized using field emission scanning electron microscope (FESEM) (Ultra plus, Carl Zeiss, Jena, Germany). The samples for FESEM analysis were prepared by the drop casting of dilute ethanolic solution of Gr-nPt composite on ITO slides. Powder x-ray diffraction (XRD) studies were carried out using Bruker aXS Model D8 Advance powder x-ray diffractometer with a Cu $K\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). The diffraction data were recorded for 2θ angles between 5° and 85° .

2.2. Chemicals and reagents

All reagents used were analar grade and used without any further purification. Graphite, hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), ethylene glycol and potassium bromide were purchased from Sigma-Aldrich (Bangalore, India). Buffer solutions of known pH in the range pH 1–12 were prepared using deionized water from MilliQ water purifier (Denvers, MA, USA) with a resistivity of not less than $18.2 \text{ M}\Omega \text{ cm}$ at $27 \pm 2^\circ\text{C}$. Arsenic stock solution (1 mM) was prepared by dissolving 0.012 g of analar grade NaAsO_2 in 100 mL distilled water. Working standards were prepared by diluting the standard stock solution on the day of analysis.

2.3. Preparation of graphene oxide and graphene–nanoplatinum composite

Graphene oxide (GO) was synthesized according to the modified Hummer's method by the exfoliation of graphite [18]. Two grams each of graphite and sodium nitrate was taken in 1 L round-bottom flask to which 100 mL of concentrated sulfuric acid was added slowly at 0°C . Twelve grams of solid potassium permanganate was added into the reaction vessel, and the reaction mixture was stirred continuously for 1 hour. Then, 400 mL of distilled water was added and the stirring was continued for another 15 minutes. Then, hydrogen peroxide (30% v/v) was added to the reaction vessel dropwise until the gas evolution completely ceases. The reaction mixture was centrifuged to separate the unexfoliated graphite from the exfoliated one. The residue was separated by decantation and washed several times using small quantities of hydrochloric acid 5% (v/v) solution, until the filtrate solution gave a negative test for the presence of sulfate with barium chloride. Then, the residue was further washed with copious amounts of double-distilled water and dried in vacuum to obtain yellow-brown solid of GO.

The Gr-nPt was prepared by the simultaneous and sequential reduction of hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and GO in one step. In order to convert GO into graphene, 5 mL solution of GO (1 mg mL^{-1} of water) and 1 mM of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ were taken in 100 mL volumetric flask and mixed thoroughly. Then, 40 mL of ethylene glycol was added and sonicated for about 1 hour to obtain homogeneous dispersion. Then, the reduction was carried out at 120°C with constant stirring under reflux conditions. The pale yellow color of the reaction mixture turns to black, which is an indication of formation of platinum nanoparticles [19]. The resulting Gr-nPt composite material was filtered and washed thoroughly with distilled water and dried in vacuum desiccator under ambient conditions. Similarly, the nanocomposite with different loadings of Pt

nanoparticles was obtained by varying the concentration of H_2PtCl_6 with the same amount of GO (1 mg mL^{-1} of water).

2.4. Modification of GCE

GCE was used as a conducting substrate for the development of the sensing platform. Prior to its modification, the GCE was polished thoroughly using 1.0, 0.3 and 0.05 μm alumina slurry and then repeatedly washed with double-distilled water followed by sonication in distilled water and ethanol for 10 minutes each. The preparation of modified electrode was carried out by the drop casting of 10 μL of aqueous colloidal dispersion of Gr-nPt (1 mg mL^{-1}) on the surface of pretreated GCE and dried at room temperature ($27 \pm 2^\circ\text{C}$).

2.5. Analytical procedure

The electrochemical determination of As(III) was carried out using SWASV in the potential range -0.2 to 0.8 V under optimized conditions. Known amounts of As(III) were taken in an electrochemical cell of 10 mL volume containing 8 mL of hydrochloric acid (1 M) as supporting electrolyte which is fitted with a tab-controlled magnetic stirrer. As(III) was preconcentrated by the electroreduction of As(III) to As(0) at a potential of -0.4 V for 80 seconds from the bulk of the electrolytic solution onto the surface of modified electrode at the interface and subsequently stripped off from the electrode surface into the bulk of the solution by scanning the potential in a positive direction after 15 seconds of equilibration time.

2.6. Sample preparation

Water samples from borewell and polluted lakes were collected and stored in polyethylene containers as per the standard protocols. The collected water samples were filtered using Whatman filter paper to remove any suspended particulate matter. After filtration, known volumes of the water samples were treated with 0.5 mL each of potassium iodide (5%) and hydrochloric acid (5 M) solutions to reduce any As(V) present in the sample to As(III). The presence of excess of iodine, indicated by pale brown color, was destroyed by adding few drops of ascorbic acid [20]. Known aliquots of these solutions were analyzed for arsenic content according to the procedure described above.

Soil samples were collected from agricultural field, dried and milled to break the lumps into fine powder. The grinded soil powder samples were sieved to get homogeneous powder. One gram of powdered sample was weighed and transferred into 100 mL beaker. To this, 2 mL of water and 0.5 g of potassium hydroxide pellets were added, and the mixture was heated on hot plate until the water evaporates and fuses. Then, it was diluted up to 100 mL, and known aliquot of this sample solution was used to determine arsenic content [21].

The tomato and spinach leaves were dried under sunlight and grinded and sieved in the form of fine powder. About 100 g of the powdered sample was placed in a 250 mL beaker, and 10 mL each of nitric and sulfuric acids was added. This content was heated to 100°C for 20 minutes in fume hood and then cooled to room temperature. To this, 10 mL of perchloric acid was added and heated again in fume hood for 5 minutes, until the dense white fumes of sulfur dioxide cease. The sample was then cooled and 1 mL of concentrated HCl was added to remove any heavy metal ions present in the sample. The solution

was heated for 15 minutes and washed with distilled water. Then, As(V) if present was reduced to As(III) by the process described as above. The solution was washed and diluted to 100 mL with distilled water in a calibrated flask. Known aliquots of the diluted solution were used for the determination of arsenic.

3. Results and discussions

3.1. Characterization of the composite

The formation of GO from native graphite and its decoration with platinum nanoparticles was characterized by studying FTIR, XRD and FESEM techniques.

The FTIR spectra of native graphite, GO and Gr-nPt composite are shown in Figure 1. The samples were uniformly mixed with KBr in 1:100 ratio using pestle and mortar and compressed into a thin pellet using pellet press. The spectra of GO (Figure 1b) showed a strong and broad band at 3250 cm^{-1} due to $-\text{OH}$ stretching vibration. The carbonyl ($-\text{C}=\text{O}$) stretching of carboxylic groups present at the edge planes of the GO sheets was observed at 1728 cm^{-1} . The absorption due to $-\text{OH}$ bending, epoxide groups and skeletal ring vibrations were observed at 1616 cm^{-1} . The deformation stretching frequency of $-\text{OH}$ groups attached to the aromatic ring was found to be at 1387 cm^{-1} [22]. However, the peaks pertaining to the oxygen-containing functional groups are absent in the spectra of graphite (Figure 1a). All these studies reveal the formation of GO from native graphite and also the generation of oxygen-containing functionalities during oxidation process. However, in case of Gr-nPt composite, the intensity of the peaks pertaining to the oxygen-containing functional groups significantly decreases, and some of the peaks are completely diminished, indicating the absence of oxygen-containing functional groups on the surface of the composite (Figure 1c). All these observations are in good agreement with the reported literature [11]. This is due to the reason that during simultaneous

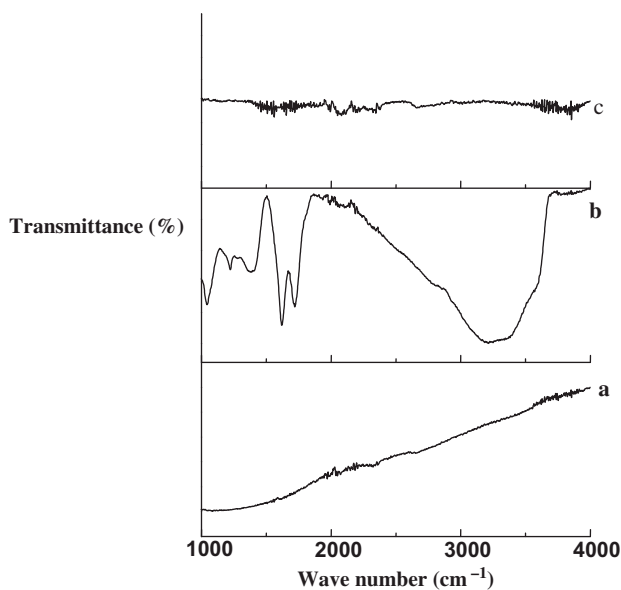


Figure 1. FTIR spectra of (a) graphitic carbon, (b) graphene oxide and (c) graphene-platinum nanocomposite (Gr-nPt).

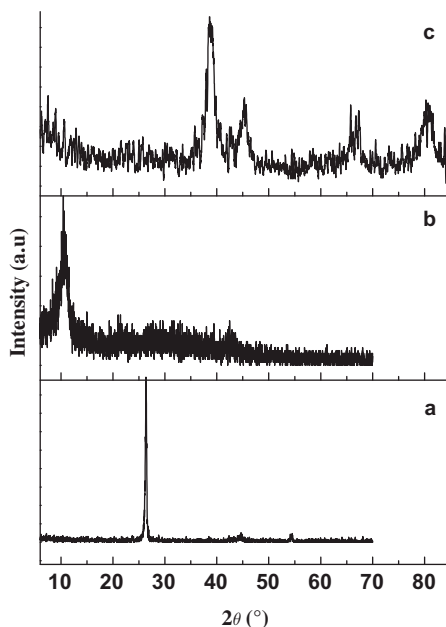


Figure 2. XRD peak patterns of (a) graphite, (b) graphene oxide and (c) graphene-platinum nanocomposite.

reduction of GO and Pt precursor in the presence of ethylene glycol as a reducing agent, all the oxygen-containing functionalities present on the surface of GO get reduced and converted into graphene material [15].

The XRD pattern of graphite, GO and Gr-nPt composite was recorded and compared to confirm the formation of GO as well as the generation of platinum nanoparticles on the layers of graphene (Figure 2). Native graphite showed a sharp peak at $2\theta = 26.34$ with a d spacing of 0.38 nm, which is a characteristic peak of graphitic carbon which corresponds to the diffraction of (002) plane. After chemical oxidation, the (002) peak of graphite has been shifted to 10.5° with a d spacing of 0.94 nm. This shift might be attributed to the introduction of oxygen-containing functional groups like epoxy, hydroxyl, carbonyl and carboxylic groups at both the sides and edges of the graphene sheets, which in turn confirms the formation of GO from natural graphite during oxidation process and also the formation of platinum particles [23].

The XRD pattern of Gr-nPt showed four peaks at 39.8° , 46.6° , 67.7° and 81.4° corresponding to the diffraction of (111), (200), (220) and (311) crystalline planes of face-centered cubic lattice of platinum, respectively [24]. It confirms the presence of platinum particles on the graphene substrate. The size and distribution of Pt nanoparticles on the surface of Gr were studied by recording the images of Pt-containing graphene sheets through FESEM. The selected region of FESEM images revealed that the particles have the size distribution between 1.25 and 6.75 nm with an average size distribution of 4 nm (Figure 3b), which is in good agreement with the XRD measurements. Enlarged portion of FESEM image showed that the Pt particles are uniformly distributed throughout the graphene layers without any agglomeration in the substrate (Figure 3a).

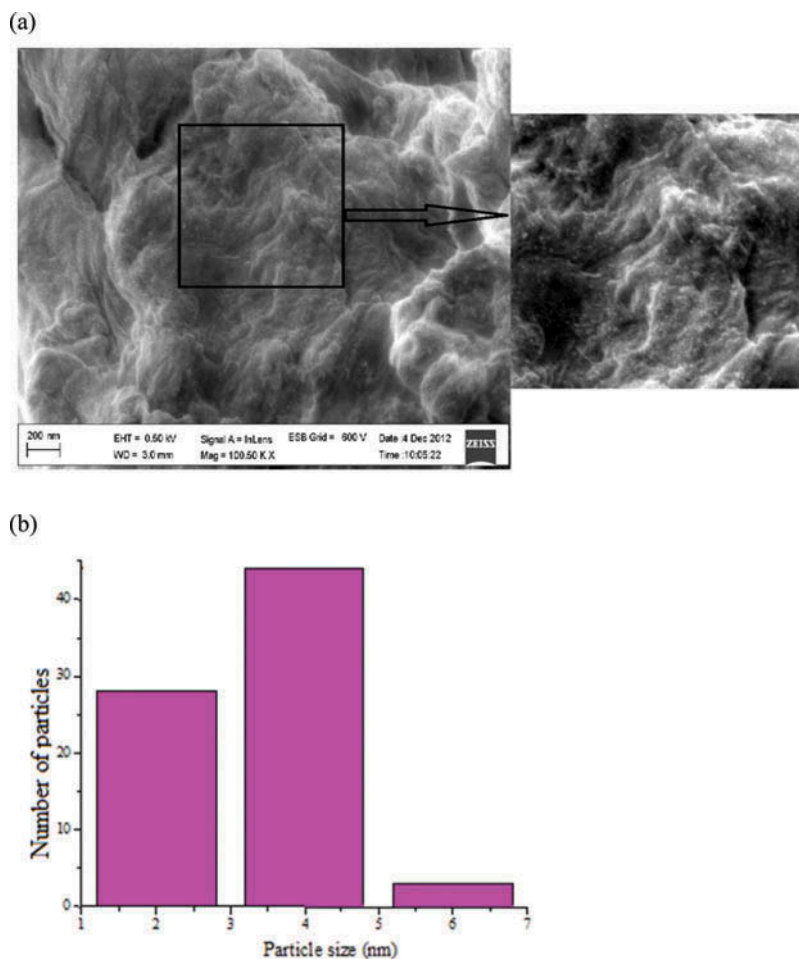


Figure 3. FESEM images of (a) graphene–platinum composite and (b) particle size profile.

3.2. Electrochemistry of As(III) at Gr–nPt-modified GCE

The electrochemical behavior of Gr–nPt-modified GCE in presence of As(III) was initially examined by using cyclic voltammetry (CV) in order to decipher the electrocatalytic activity of Gr–nPt composite toward arsenic. Cyclic voltammetric profile of 10 μM of As(III) in 1 M HCl at graphene and Gr–nPt-modified electrode in the potential range from 0.6 to 0.6 V with a scan rate 50 mV sec^{-1} is shown in Figure 4. The graphene-modified GCE did not show any voltammetric signature for the presence of arsenic in the potential window used in the present investigation. This indicates that the graphene alone is not capable of favoring the redox process for arsenic; hence, it is insensitive and not useful material for the construction of sensing platform in arsenic measurement. Whereas Gr–nPt composite-modified GCE showed a voltammetric peak in the forward cathodic sweep at -0.18 V which can be ascribed to the three-electron reduction process of As(III) to As(0), and in the reversal anodic sweep an intense peak at 0.16 V was observed which corresponds to reoxidation (stripping) of As(0) to As(III). The potential required for the reduction of As(III) to As(0) is much less negative than that observed on Pt and Au

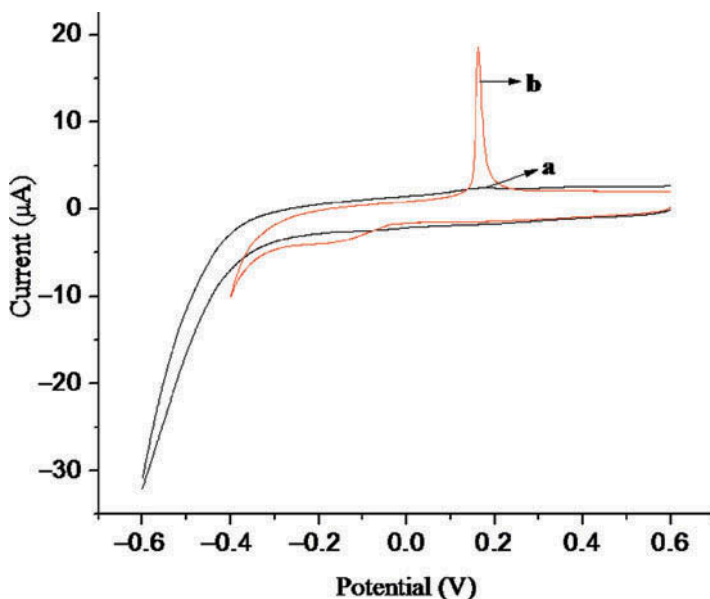


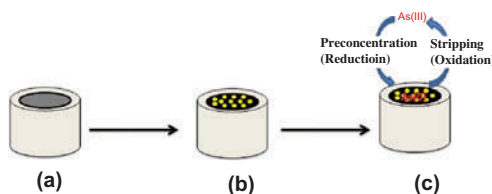
Figure 4. Overlaid cyclic voltammograms recorded at (a) graphene and (b) Gr-nPt composite-modified glassy carbon electrodes in 1 M HCl in the presence of 10 μM As(III). Scan rate -50 mV sec^{-1} .

nanoparticle-modified GCE [24,25]. These observations revealed that the arsenic reduction process is more favorable at Gr-nPt-modified GCE with low overpotential. Such voltammetric response was not observed in graphene, showing that the observed response at Gr-nPt electrode is due to the presence of Pt nanoparticles. Hence, Gr-nPt composite-modified GCE showed potential affinity toward arsenic, and therefore, the feasible redox reaction of As(III) and the enhancement in the peak current can be attributed to the high electrocatalytic activity of the platinum nanoparticles toward As(III).

It is evident from the Figure 4 that the oxidation peak (stripping) is sharper and more significant than the corresponding reduction peak; hence, the oxidation peak was systematically studied using SWASV in order to achieve the desired detection limit. The stripping voltammetric determination of arsenic proceeds through the following two steps.

- (1) Preconcentration of As(III) from the bulk of the electrolytic solution onto the modified electrode surface under the applied potential of -0.4 V for preselected time of 80 seconds under constant stirring.
- (2) Stripping (oxidation) of As(0) from the electrode surface into the bulk of the electrolytic solution as As(III). This anodic stripping step generates quantifiable analytical signal, and the signal current has been correlated to the arsenic concentration.

The general scheme for the preconcentration and stripping of arsenic into the electrolytic solution has been shown in the Scheme 1. In a typical stripping voltammogram of arsenic measurement (data not shown), the Gr-nPt composite electrode did not show any voltammetric peak in the absence of arsenic in the potential window used in present study. Hence, it can be applied for the quantification of analytes (metal ions) which are



Scheme 1. Schematic pathway of arsenic detection. (a) Bare glassy carbon electrode. (b) Glassy carbon electrode modified with Gr-nPt composite. (c) Electrocatalysis of As(III) at Gr-nPt interface.

active in this potential region. Whereas in the presence of arsenic, it showed a well-defined and sharp oxidation peak at 0.14 V, indicating that the Gr-nPt-modified GCE showed potential affinity toward arsenic, and hence this kind of modified electrode can be used for the electrochemical measurement of arsenic at very low concentration level.

3.3. Optimization study

In order to obtain maximum efficiency of the proposed electrode toward the electrochemical measurement of arsenic, the reaction variables like platinum loading, electrolytic solution, deposition potential and deposition time which controls the analytical response have been optimized.

The amount of platinum nanoparticles present on the graphene layers plays a very important role in the electrochemical determination of arsenic as they behave as catalyst for the redox process of arsenic. Therefore, the Gr-nPt of different loadings of platinum nanoparticles was prepared by varying the concentration of H_2PtCl_6 from 0.2 to 1.4 mM with the same amount of GO (1 mg mL^{-1} of water). The electrochemical performance of each composite has been studied with respect to As(III) using CV. The cyclic voltammetric response increases with increase of platinum loading up to 1 mM; thereafter, there is no significant improvement in the electrochemical performance of arsenic. Therefore, platinum loading of 1 mM of H_2PtCl_6 has been used in the composite preparation.

The shape and sensitivity of the stripping peak in any voltammetric experiment mainly depend on the diffusion of the analyte species from bulk of the electrolytic solution toward the interface and vice versa. The diffusion toward the electrode surface depends on the surface structure and the diffusion from the surface into the bulk of the solution depends on the ions of the electrolytic solution, which show potential interacting ability toward the metal ion present at the interface to form their respective compounds. The Cl^- ions present in the HCl solution show a strong affinity toward ionic arsenic, resulting through oxidation at the interface to form AsCl_3 species [26]. Hence the choice of supporting electrolyte governs the magnitude of the stripping current generated at the electrode interface. Hence, the electrochemical response of arsenic at Gr-nPt composite-modified GC electrode has been examined in the presence of some of the commonly used electrolytes like HCl, H_2SO_4 and HNO_3 at different concentration levels (Figure 5) [27]. Among these, HCl showed well-defined sharp and intense peak in comparison with other electrolytes. The concentration of HCl was varied in the concentration range 0.1 to 2 M, and it was found that the peak current increases from 0.1 to 1 M and then it decreases. The increase of peak current might be due to the effective complexing ability of Cl^- ions with As(III) and the decrease of peak current might be due to the adsorption of Cl^- ions on Pt

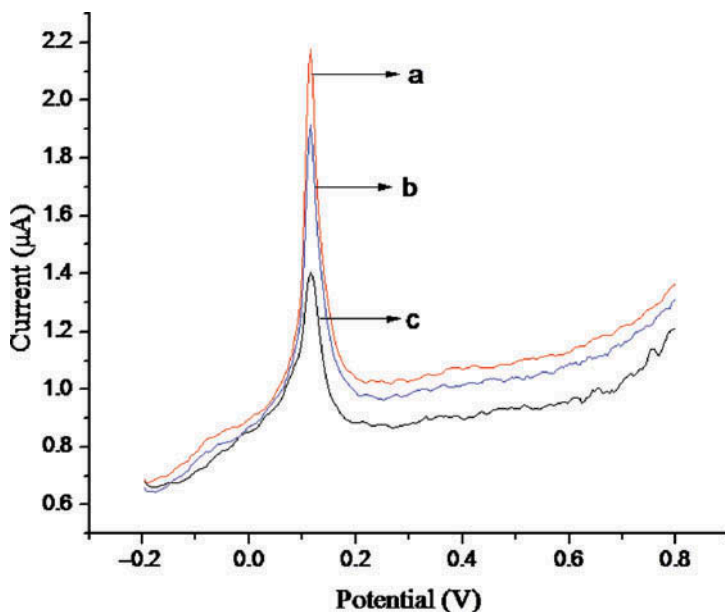


Figure 5. Overlaid stripping voltammograms of 50 nM of As(III) present in 1 M (a) HCl, (b) HNO₃ and (c) H₂SO₄.

surface at higher concentration level [28,29]. In case of H₂SO₄, least stripping response was noticed which might be due to the bulky and less complexing nature of SO₄²⁻ ions, which results lower coordination number with As(III). Thus, more energy might be required for its dissociation [27]. The peak intensity observed in the presence of hydrochloric acid as an electrolytic solution was better than nitric acid and sulfuric acids. Hence, hydrochloric acid (1 M) has been used as an optimum electrolyte throughout the study.

The effect of applied potential on the reduction of As(III) to As(0) at the modified interface by holding the electrode at a particular potential was studied. It is well known that higher reduction potential values can be expected to give the maximum current due to the reduction of more and more As(III) ions. Therefore, the dependence of peak current with respect to deposition potential was studied from -0.1 to -0.6 V (Figure 6). The peak current increases with increase of potential from -0.1 to -0.4 V and then decreases. The decrease of peak current is attributed to the inefficient deposition of arsenic. This might be due to the reason that at more cathodic potentials, the water molecules compete with arsenic to undergo reduction and result in the formation of H₂ gas which further blocks the surface and decreases the current response. In addition to this, at more cathodic potentials, some of the elemental arsenic can be converted into As³⁻ [25]. Due to this, a deposition potential of -0.4 V was used as an optimum potential in all further studies. The time required for the accumulation of As(III) from the bulk of the electrolyte solution onto the surface of the Gr-nPt-modified electrode plays a crucial role in trace level estimations. Therefore, the dependence of peak current with respect to the preconcentration time is studied from 20 to 120 seconds (Figure 7). It has been found that the peak current increases with an increase of preconcentration time from 20 to 80 seconds, and then it

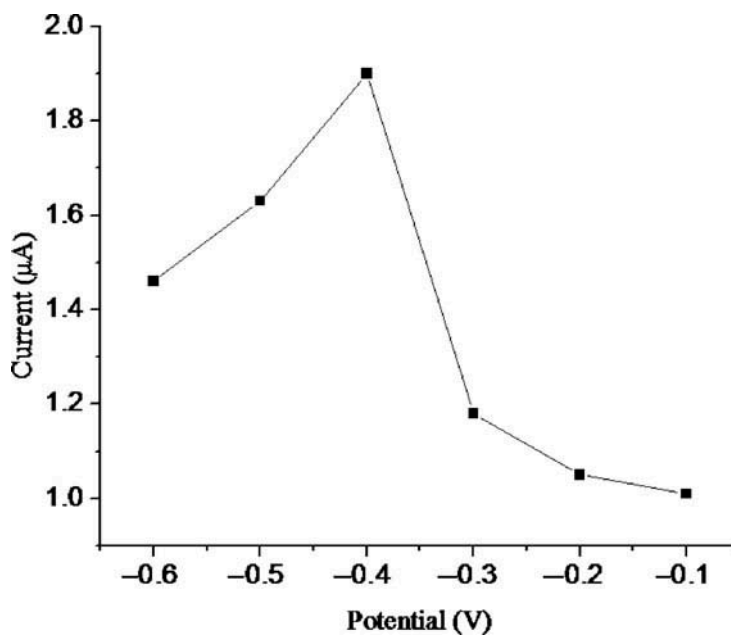


Figure 6. Effect of deposition potential on the stripping peak current obtained for 50 nM of As(III) present in 1 M HCl with a deposition time of 80 seconds.

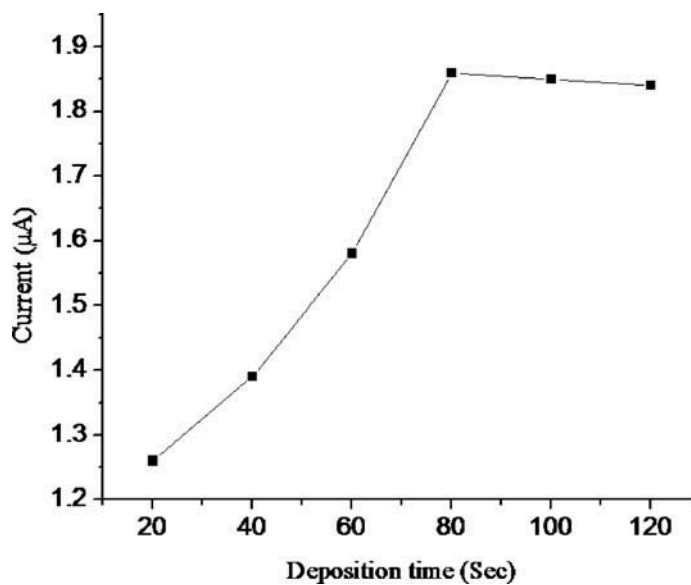


Figure 7. Effect of deposition time on the stripping peak current obtained for 50 nM of As(III) present in 1 M HCl with a deposition potential of -0.4 V.

remained constant. This might be due to the saturation response of arsenic on the electrode at higher concentration as it is a nonconducting semiconductor and does not easily deposit on itself [30].

3.4. Analytical merits

The calibration plot was constructed by measuring the peak currents produced by the stripping of arsenic with the successive addition of 10 nM of As(III) into an electrochemical cell of 10 mL volume under optimized conditions. The Gr-nPt-modified electrode showed a linear response in the concentration range up to 100 nM (Figure 8) with a detection limit of 1.1 nM which is well below the threshold limit value of arsenic in drinking water prescribed by WHO [3].

The proposed sensor has been compared with some of the existing electrodes used for arsenic measurement in terms of detection limits (Table 1). It signifies the importance of the proposed sensor prepared using Gr-nPt composite in the detection of As(III). The proposed sensor provides comparably low detection limits; hence, it can be used as an alternative tool to the existing protocols.

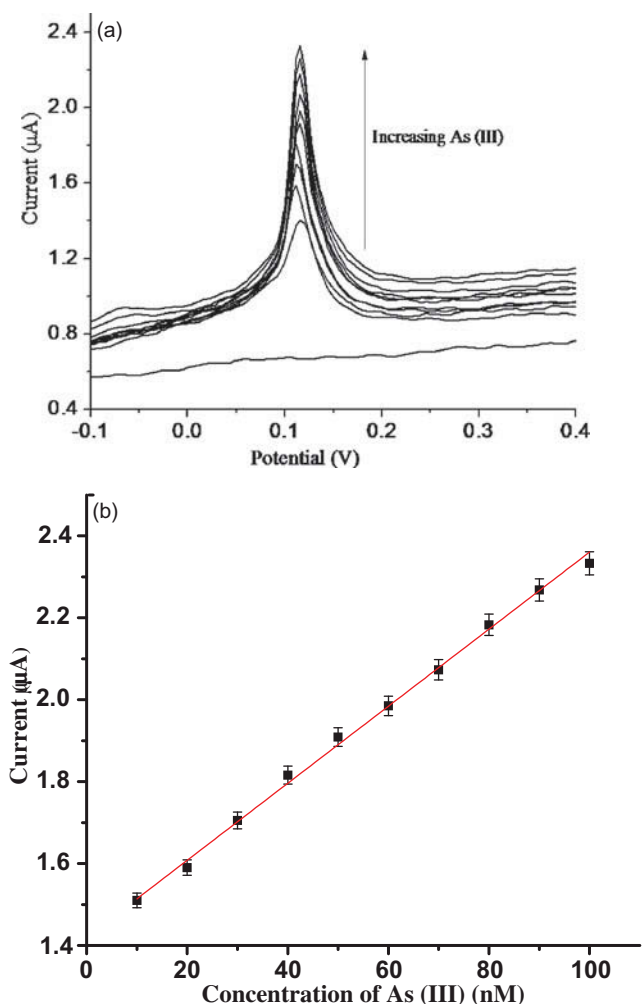


Figure 8. (a) Overlaid square-wave anodic stripping voltammograms of As(III) under optimized conditions and (b) calibration plot.

Table 1. Comparison of few existing electrodes with the proposed electrode in As(III) measurement.

Modified carbon electrodes	Method	Limit of detection (LOD)	Linear range	Reference
Pt-GCE	DPASV	0.48 μM	1–50 μM	[25]
Au-GC/BPPG	CV	0.8 μM	2–12 μM	[31]
Pt-Pd-Polymer/GCE	DPASV	2.4 μM	0–6 mM	[32]
Co oxide-GCE	CV	11 μM	0–4 μM	[33]
rGO-PbO/GCE	SWASV	0.01 μM	0.1–0.1 nM	[34]
Gr-nPt/GC	SWASV	1.1 nM	10–100 nM	Present study

Notes: Pt, platinum nanoparticles; Au, gold nanoparticles; Pd, palladium nanoparticles; Co, cobalt; GC, glassy carbon spheres; GCE, glassy carbon electrode; CNT, carbon nanotubes; BPPG, basal plane pyrolytic graphite; rGO, reduced graphene oxide; PbO, lead oxide; Gr-nPt, graphene platinum nanoparticles; CV, cyclic voltammetry; LSV, linear sweep voltammetry; DPASV, differential pulse anodic stripping voltammetry; SWASV, square-wave anodic stripping voltammetry.

Precise and selective measurement of arsenic present in real sample matrices is a challenging task, as the other commonly encountered cations and anions normally present in the real samples along with arsenic may also get deposited and stripped off from the electrode surface under the same optimized conditions used in the present study. The efficiency of the proposed sensor electrode toward arsenic quantification has been examined in the presence of 50 nM of arsenic along with different concentrations of different ions. The tolerance limits of these ions in the present investigation have been listed in Table 2. Above these tolerance limits, the added ions interfere and alter the peak currents produced by the stripping of arsenic. The developed sensor has showed least interference from most of the common ions due to specific and selective interaction of the Gr-nPt composite with As(III) ions. Hence, this sensor can be used for the selective quantification of arsenic from most of the real sample matrices without any significant interference from other ions.

The validation of the proposed electrode using Gr-nPt composite on the surface of GCE toward As(III) measurement has been examined by applying it to the real sample matrices like borewell, polluted water, agricultural soil, spinach and tomato leaf samples. Known quantities of As(III) were added, and its recovery study was carried out. The proposed electrode showed a linear range up to 100 nM, which is well within the limits of As(III) present in the real sample matrices whose compositions are given in Table 3. Hence, the modified electrode of this kind can be used to quantify As(III) from a variety of water samples as well as vegetable samples.

For practical applications, reproducibility of the analytical results is very important as they require very accurate and precise measurement. Therefore, the reproducibility has been examined by using the same electrode for 15 repetitive measurements in 1 M HCl as supporting electrolyte solution containing 50 nM of As(III) under identical conditions.

Table 2. Interference study.

Interferents	Tolerance limit (μM)
Pb ²⁺ , Cd ²⁺ , Cu ²⁺ , Hg ²⁺	100
Ba ²⁺ , Ca ²⁺ , Zn ²⁺ , Ni ²⁺ , Co ²⁺ , Fe ²⁺	380
Cl ⁻ , F ⁻ , I ⁻ , Br ⁻	450
Na ⁺ , K ⁺ , Fe ³⁺	620

Table 3. Determination of As(III) from different environmental sample matrices.

Sample	Originally present arsenic (nM)	Added arsenic (nM)	Total arsenic found (nM)	Recovery (%)
Polluted water	50	10	59.78	99.63
Borewell water	17	10	27.03	100.11
Soil extract	35	10	45.14	100.31
Tomato leaves	12	10	21.83	99.22
Spinach leaves	20	10	30.02	100.06

The relative standard deviation for all these measurements was found to be $\pm 4.6\%$. Similarly, the reproducibility of the results has been checked using four different electrodes of similar kind. The relative standard deviation for all these measurements was found to be $\pm 5\%$. These results indicate that the analytical performance of the fabricated electrode is highly reproducible; hence the proposed sensor can be used for several repetitive measurements with good accuracy and precision in its electrocatalytic activity toward arsenic determination.

4. Conclusions

A simple protocol for the chemical modification of graphene with platinum nanoparticles has been described using a mild and environmental friendly reducing agent, i.e., ethylene glycol. The method has resulted in the formation of platinum nanoparticles with an average particle size of 4 nm. The prepared Gr-nPt composite has been used as a sensing platform in the determination of arsenic at nanomolar level from real sample matrices without any severe interference from common cations and anions. The lowest detection limit obtained can be attributed to the superior electrocatalytic activity of platinum nanoparticles present on the graphene layers. The fabricated electrode is quite stable and can be used for repetitive analytical measurements.

Acknowledgments

The authors acknowledge the Department of Science & Technology (DST), New Delhi, India, for the financial support and award of fellowship to G.K. Raghu. The authors are extremely thankful to Prof. K.R. Nagasundara, Department of Chemistry, Bangalore University for providing hexachloroplatinic acid. The authors also express their gratitude to Prof. V. Lakshminarayanan, Raman Research Institution, Bangalore, for useful discussions during the manuscript preparation.

References

- [1] F. Arduini, J.Q. Calvo, G. Palleschi, D. Moscone, and A. Amine, *Bismuth-modified electrodes for lead detection*, Trends Anal. Chem. 29 (2010), pp. 1295–1304. doi:10.1016/j.trac.2010.08.003.
- [2] A. Cavicchioli, M.A. La Scalea, and I. Gutz, *Analysis and speciation of traces of arsenic in environmental, food and industrial samples by voltammetry: A review*, Electroanalysis. 16 (2004), pp. 697–711. doi:10.1002/elan.200302936.
- [3] World Health Organization, *Arsenic in drinking water*, Fact sheet No. 210 Revised May 2001.
- [4] M.D. Luh, R.A. Baker, and D.E. Henley, *Arsenic analysis and toxicity – A review*, Sci. Total Environ. 2 (1973), pp. 1–12.

- [5] M. Khairy, R.O. Kadara, D.K. Kampouris, and C.E. Banks, *In situ bismuth modified screen printed electrodes for the bio-monitoring of cadmium in oral (saliva) fluid*, Anal. Methods. 2 (2010), pp. 645–649.
- [6] R. Feeney and S.P. Kounaves, *On-site analysis of arsenic in groundwater using a micro-fabricated gold ultramicroelectrode array*, Anal. Chem. 72 (2000), pp. 2222–2228. doi:10.1021/ac991185z.
- [7] M.C. Daniel and D. Astruc, *Gold nanoparticles: Assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology*, Chem. Rev. 104 (2004), pp. 293–346. doi:10.1021/cr030698.
- [8] R. Narayanan and M.A. El-Sayed, *Catalysis with transition metal nanoparticles in colloidal solution: Nanoparticle shape dependence and stability*, J. Phys. Chem. B. 109 (2005), pp. 12663–12676. doi:10.1021/jp051066p.
- [9] M.M.O. Thotiyil, H. Basit, J.A. Sánchez, C. Goyer, L. Coche-Guerente, P. Dumy, S. Sampath, P. Labbé, and J. Moutet, *Multilayer assemblies of polyelectrolyte-gold nanoparticles for the electrocatalytic oxidation and detection of arsenic(III)*, J. Colloid Interface Sci. 383 (2012), pp. 130–139. doi:10.1016/j.jcis.2012.06.033.
- [10] B.K. Jena and C.R. Raj, *Gold nanoelectrode ensembles for the simultaneous electrochemical detection of ultratrace arsenic, mercury, and copper*, Anal. Chem. 80 (2008), pp. 4836–4844. doi:10.1021/ac071064w.
- [11] R.S. Dey and C.R. Raj, *Development of an amperometric cholesterol biosensor based on graphene-Pt nanoparticle hybrid material*, J. Phys. Chem. C. 114 (2010), pp. 21427–21433. doi:10.1021/jp105895a.
- [12] H. Cui, W. Yang, X. Li, H. Zhao, and Z. Yuan, *An electrochemical sensor based on a magnetic Fe₃O₄ nanoparticles and gold nanoparticles modified electrode for sensitive determination of trace amounts of arsenic(III)*, Anal. Methods. 4 (2012), pp. 4176–4181. doi:10.1039/c2ay25913c.
- [13] Q.X. Zhang and L.B. Yin, *Electrochemical performance of heterostructured Au–Pd bimetallic nanoparticles toward As(III) aqueous media*, Electrochem. Commun. 22 (2012), pp. 57–60. doi:10.1016/j.elecom.2012.05.025.
- [14] D.A.C. Brownson, D.K. Kampouris, and C.E. Banks, *Graphene electrochemistry: Fundamental concepts through to prominent*, Chem. Soc. Rev. 21 (2012), pp. 6944–6976. doi:10.1039/c2cs35105f.
- [15] C. Xu, X. Wang, and J. Zhu, *Graphene – Metal particle nanocomposites*, J. Phys. Chem. C. 112 (2008), pp. 19841–19845. doi:10.1021/jp807989b.
- [16] P.V. Kamath, *Virtual graphene*, Analyst. 19 (2010), pp. 100–125.
- [17] S. Guo, D. Wen, Y. Zhai, S. Dong, and E. Wang, *Platinum nanoparticle ensemble-on-graphene hybrid nanosheet: One-pot, rapid synthesis, and used as new electrode material for electrochemical sensing*, ACS Nano. 4 (2010), pp. 3959–3968. doi:10.1021/nn100852h.
- [18] W.S. Hummers and R. Offeman, *Preparation of graphitic oxide*, J. Am. Chem. Soc. 80 (1958), pp. 1339–1342. doi:10.1021/ja01539a017.
- [19] Y. Li, W. Gao, L. Ci, C. Wang, and P.M. Ajayan, *Catalytic performance of Pt nanoparticles on reduced graphene oxide for methanol electro-oxidation*, Carbon. 48 (2010), pp. 1124–1130. doi:10.1016/j.carbon.2009.11.034.
- [20] E. Kavlentis, *Spectrophotometry determination of arsenic(III) and antimony(III) by means of isonicotinoyl hydrazones of 4-dimethylaminobezaldehyde (4-DBIH) and 2-hydroxynaphthaldehyde (2-HNIH)*, Anal. Lett. 20 (1987), pp. 2043–2047. doi:10.1080/00032718708078044.
- [21] M. Pandurangappa and K. Sureshkumar, *Trace level arsenic quantification through methyl red bromination*, Am. J. Anal. Chem. 3 (2012), pp. 455–461. doi:10.4236/ajac.2012.37060.
- [22] S. Stankovich, D.A. Dikin, R.D. Piner, K.A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S.T. Nguyen, and R.S. Ruoff, *Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide*, Carbon. 45 (2007), pp. 1558–1565. doi:10.1016/j.carbon.2007.02.034.
- [23] G.K. Ramesha and S. Sampath, *Exfoliated graphite oxide modified electrode for the selective determination of picomolar concentration of lead*, Electroanalysis. 19 (2007), pp. 2472–2478. doi:10.1002/elan.200704005.
- [24] H.-W. Ha, I.Y. Kim, S.-J. Hwang, and R.S. Ruoff, *One-pot synthesis of platinum nanoparticles embedded on reduced graphene oxide for oxygen reduction in methanol fuel cells*, Electrochem. Solid State Lett. 14 (2011), pp. 70–73. doi:10.1149/1.3584092.

- [25] X. Dai and R.G. Compton, *Detection of As(III) via oxidation to As(V) using platinum nanoparticle modified glassy carbon electrodes: Arsenic detection without interference from copper*, *Analyst*. 131 (2006), pp. 516–521. doi:10.1039/b513686e.
- [26] X. Dai, O. Nekrassova, M.E. Hyde, and R.G. Compton, *Anodic stripping voltammetry of arsenic (III) using gold nanoparticle-modified electrodes*, *Anal. Chem.* 76 (2004), pp. 5924–5929. doi:10.1021/ac049232x.
- [27] E. Majid, S. Hrapovic, Y. Liu, K.B. Male, and J.H.T. Luong, *Electrochemical determination of arsenite using a gold nanoparticle modified glassy carbon electrode and flow analysis*, *Anal. Chem.* 78 (2006), pp. 762–769. doi:10.1021/ac0513562.
- [28] A. Profumo, M. Fagnoni, D. Merli, E. Quartarone, S. Protti, D. Dondi, and A. Albini, *Multiwalled carbon nanotube chemically modified gold electrode for inorganic as speciation and Bi(III) determination*, *Anal. Chem.* 78 (2006), pp. 4194–4199. doi:10.1021/ac060455s.
- [29] R. Feeney and S. Kounaves, *On-site analysis of arsenic in groundwater using a microfabricated gold ultramicroelectrode array*, *Anal. Chem.* 72 (2000), pp. 2222–2228. doi:10.1021/ac991185z.
- [30] P. Davis, G. Dulude, R. Griffin, W.R. Matson, and E.W. Zink, *Determination of total arsenic at the nanogram level by high-speed anodic stripping voltammetry*, *Anal. Chem.* 50 (1978), pp. 137–143. doi:10.1021/ac50023a031.
- [31] R. Baron, B. Sljukic, C. Salter, A. Crossley, and R.G. Compton, *Electrochemical detection of arsenic on a gold nanoparticle array*, *Phys. Chem. Nanoclust. Nanomat.* 81 (2007), p. 1443.
- [32] J.A. Sánchez, B.L. Rivas, S.A. Pooley, L. Basaez, E. Pereira, I.P. Paintrand, C. Bucher, G. Royal, E.S. Aman, and J.C. Moutet, *Electrocatalytic oxidation of As(III) to As(V) using noble metal-polymer nanocomposites*, *Electrochim. Acta.* 55 (2010), pp. 4876–4882. doi:10.1016/j.electacta.2010.03.080.
- [33] A. Salimi, H. Mamkhezri, R. Hallaj, and S. Soltanian, *Electrochemical detection of trace amount of arsenic(III) at glassy carbon electrode modified with cobalt oxide nanoparticles*, *Sens. Actuat. B Chem.* 129 (2008), pp. 246–254. doi:10.1016/j.snb.2007.08.017.
- [34] G.K. Ramesha and S. Sampath, *In-situ formation of graphene – lead oxide composite and its use in trace arsenic detection*, *Sensors Actuat. B Chem.* 160 (2011), pp. 306–311. doi:10.1016/j.snb.2011.07.053.