

# Voltammetric Analysis of As(III) at a Cobalt Nanoparticles/Reduced Graphene Oxide Modified Exfoliated Graphite Electrode

A Jimana<sup>1</sup>, MG Peleyeju<sup>1</sup>, L Tshwenya<sup>1</sup>, K Pillay<sup>1</sup>, OA Arotiba<sup>1,2,\*</sup>

<sup>1</sup> Department of Applied Chemistry, University of Johannesburg, South Africa

<sup>2</sup> Centre for Nanomaterials Science Research, University of Johannesburg, South Africa

\*E-mail: [oarotiba@uj.ac.za](mailto:oarotiba@uj.ac.za)

Received: 6 June 2018 / Accepted: 10 August 2018 / Published: 1 October 2018

---

This work presents the detection and quantification of As(III) at an exfoliated graphite electrode (EG) modified with a composite of cobalt nanoparticles and reduced graphene oxide. The materials were characterised by Raman spectroscopy and scanning electron microscopy & energy dispersive spectroscopy. Modification of the surface of EG with the composite material led to significant improvement in its electro-active surface area and thus electrocatalytic activity. The sensor was utilised for the voltammetric analysis of As(III) in standard and real samples and the limit of detection and limit of quantification were found to be 0.31 and 1.01 ppb respectively, under optimum conditions. The proposed device can be employed for practical analytical purposes.

---

**Keywords:** Arsenic, voltammetric detection, cobalt nanoparticles, reduced graphene oxide, exfoliated graphite electrode.

## 1. INTRODUCTION

Increasing industrial activities has birthed pollution of water bodies, leaving many countries around the world to face the challenge of fresh water scarcity. A major group of water pollutants are the heavy metals including Pb, Cd, Cr, Ni, As etc [1, 2]. Mining activities contribute significantly to heavy metals load in the environment, and this presents risks to both humans and animals owing to the toxicity of these heavy metals [3]. Long-term exposure to arsenic, for instance, can cause hyperkeratosis, irregular heartbeat and different forms of cancers in humans [4, 5]. The maximum concentration of arsenic allowed in drinking water according to the World Health Organization (WHO) is 10 ppb [6]. It is therefore necessary to develop devices to monitor the level of arsenic in surface and

ground waters since these sources of water are the ones readily available to a large population of humans in the rural areas. Electrochemical sensors are well suited for this purpose given their considerable sensitivity, ease of operation and portability amongst others [7]. An electrochemical sensor is particularly suitable for on-site analysis since it is portable and does not require specially trained individuals to operate it. This is in contrast to spectrometric equipment that are heavy and require skilled personnel to handle.

Many authors have proposed different electrochemical sensors for determination of As(III) in water samples. Very recently, Bhanjana et al. reported a graphite pencil modified SnO<sub>2</sub> nanoneedles as sensing platform for As(III) in standard and real samples [8]. Carrera et al. also developed carbon fiber microelectrode modified with Au nanoparticles for the detection of As in tap and well waters [9]. Similarly, Yuan et al. modified a gold electrode with a composite of trithiocyanuric acid and reduced graphene oxide and employed the platform for the sensitive qualitative and quantitative analysis of As in tap and river samples [10]. Also, Rodríguez et al. utilised ZrO<sub>2</sub> thin film loaded with Au nanoparticles for the detection of As in water [11]. In all these reports the authors explored the adsorption characteristics and the electrocatalytic activities of their chosen platforms to develop sensors for As in water samples.

Voltammetric detection of both organic and inorganic analytes at modified exfoliated graphite electrodes has been reported [12-14]. Exfoliated graphite offers considerable conductivity, can be easily modified and the surface can be regenerated. In this work, we present an As(III) sensor designed by modifying the surface of exfoliated graphite with a nanocomposite of cobalt nanoparticles and reduced graphene oxide (rGO). Both materials exhibit required characteristics for the determination of As in both standard and real water samples.

## 2. METHODOLOGY

### 2.1 Reagents and materials

HNO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, DMF, KMnO<sub>4</sub>, NaNO<sub>3</sub>, NaOH, CoCl<sub>2</sub>, K<sub>3</sub>[Fe(CN)<sub>6</sub>], K<sub>4</sub>[Fe(CN)<sub>6</sub>], arsenic standard, natural graphite flakes (NGF), natural graphite powder, were all purchased from Sigma Aldrich, South Africa. Conductive silver paint, epoxy resin, copper wire and glass rods were procured from local stores. All the chemicals were of analytical grade and deionised water was used for the preparation of all solutions.

### 2.2 Preparation of EG and EG electrode

EG was prepared following a procedure reported earlier [15, 16]. Preparation of EG electrode was achieved according to a method by Arotiba and co-workers [17]. Approximately 1 g of the prepared exfoliated graphite was compressed into pellets of 5 mm in diameter at a high pressure using hydraulic press. A previously cleaned copper wire (diameter 1 mm) was coiled into a flat surface to obtain exactly 5 mm diameter to accommodate the formed EG pellet. A conductive silver paint was

then dropped onto the surface of the coiled wire and one EG pellet was placed on top of it. It was allowed to dry at room temperature for a few hours. The edges of the pellet were covered with non-conductive epoxy resin and with teflon tape, leaving only the base exposed. The straight portion of the wire was inserted into a glass rod (a small portion is left for electrical contact) and sealed.

### 2.3 Preparation of rGO and Co-rGO composite

Graphene oxide was synthesised from graphite using modified Hummer's method. Approximately 2g of natural graphite powder and 2 g of  $\text{NaNO}_3$  were mixed in a 50 mL of  $\text{H}_2\text{SO}_4$ . The mixture was stirred for 2 h, and 6 g of potassium permanganate was added slowly to the mixture while the reaction was kept at a temperature lower than 15 °C in an ice bath. The reaction was subsequently stirred at room temperature for 12 h after which about 100 mL of deionized water was added and the reaction temperature increased to 98 °C. An additional 200 mL of deionized water was added to the mixture while the solution was continuously stirred. The reaction was then terminated by adding 10 mL of  $\text{H}_2\text{O}_2$  and the mixture turned yellow. The GO slurry was washed with 10% HCl and deionized water severally by centrifugation. The obtained material was filtered and dried at 45 °C for 24 h. The grey powder obtained was kept for use. Reduction of GO was achieved using hydrazine.

A method adapted from Ji et al [18] was used for the preparation of Co-rGO nanocomposite: A solution of 35 mg of GO dispersed in 80 mL of ethylene glycol was prepared and sonicated for 1 h. The dispersion was then mixed with 20 mL of ethylene glycol solution of  $\text{CoCl}_2$ . Subsequently, 0.8 mL of 85% hydrazine hydrate and 3.6 mL of ethylene glycol solution of NaOH were added to the mixture. After ultra-sonication for 10 min, the mixture was then transferred into a 250 mL round-bottom flask and refluxed at 110 °C for 3 h under  $\text{N}_2$  atmosphere. The solid material was separated and washed by centrifugation with water and absolute ethanol successively to remove any impurities. It was then dried in a vacuum oven at 50 °C for 24 h.

### 2.4 Modification of EG electrode with rGO and Co-rGO

To modify the EG with rGO or Co-rGO, a measured amount of the rGO or its composite was dispersed in DMF and thoroughly mixed. A 20  $\mu\text{L}$  of the dispersion was then coated on the surface of the EG electrode with micropipette. The modified electrode was left to dry under normal room conditions for 3 h. The surface of the EG electrode was regenerated by polishing with emery sheet and rinsing with water.

### 2.5 Electrochemical measurements

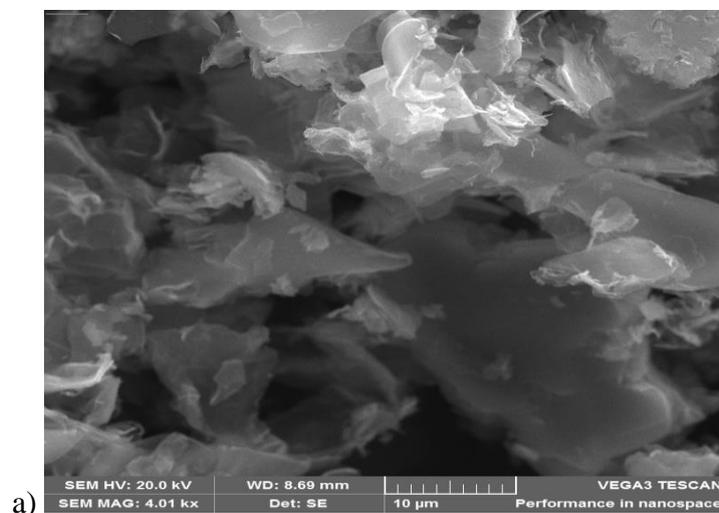
All electrochemical measurements were performed on Autolab potentiostat (PGSTAT 302N) using a three-electrode system. Exfoliated graphite (and modified exfoliated graphite), Ag/AgCl (3M KCl), and platinum wire were used as working, reference and counter electrodes respectively. The working electrode has a diameter of 5 mm. All the experiments were conducted at approximately 25

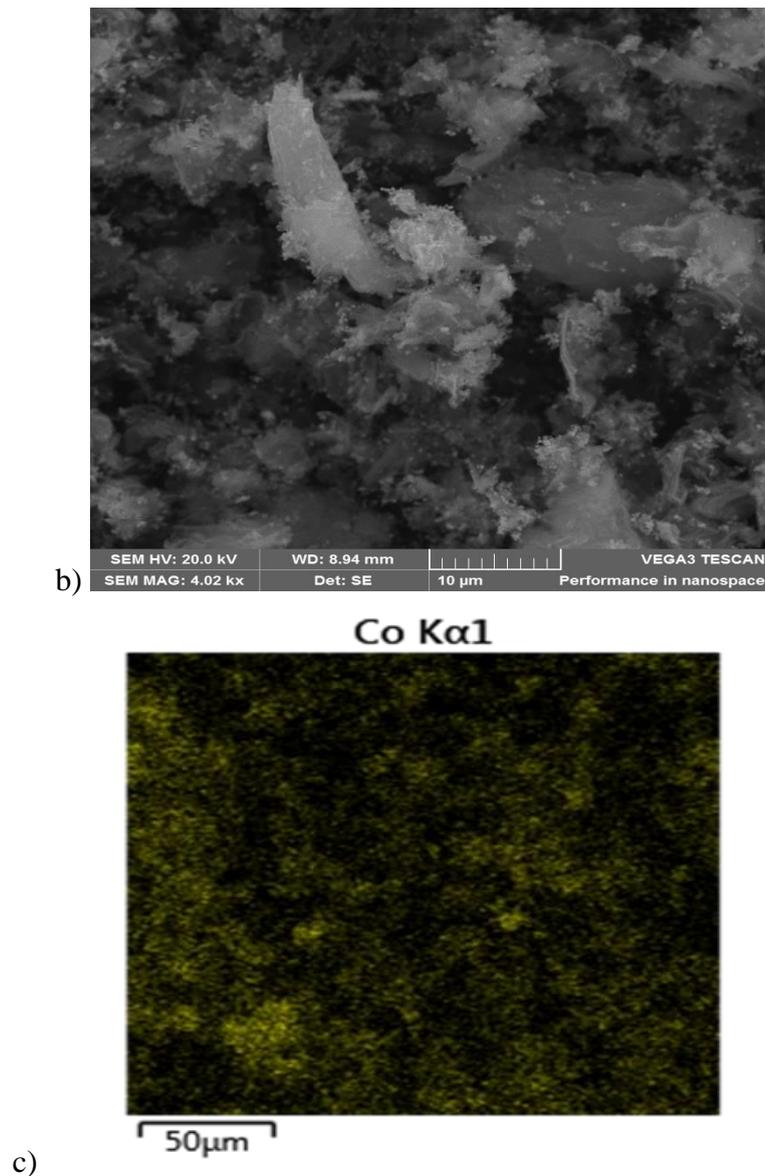
°C. All solutions for electrochemical analyses were purged with pure argon gas for at least 10 min before each analysis. Square wave anodic stripping voltammetry (SWASV) method was used for the electrochemical detection of As(III).

### 3. RESULTS AND DISCUSSION

#### 3.1 Scanning electron microscopy and energy dispersive spectroscopy

The images of the rGO and Co-rGO were obtained on a scanning electron microscope. Fig. 1a presents the image of rGO, graphene sheets can be readily seen in this image. In fig 1b, particles can be seen to be evenly distributed on the graphene sheets. EDS elemental mapping (Fig. 1c) reveals the presence of Co particles in the composite material. It is important to note that it is possible for rGO sheets to restack after reduction process has taken place due to strong van der Waals interaction, rendering them not so effective [19]. Introduction of metal nanoparticles can prevent the sheets from restacking and hence preserving its unique properties..

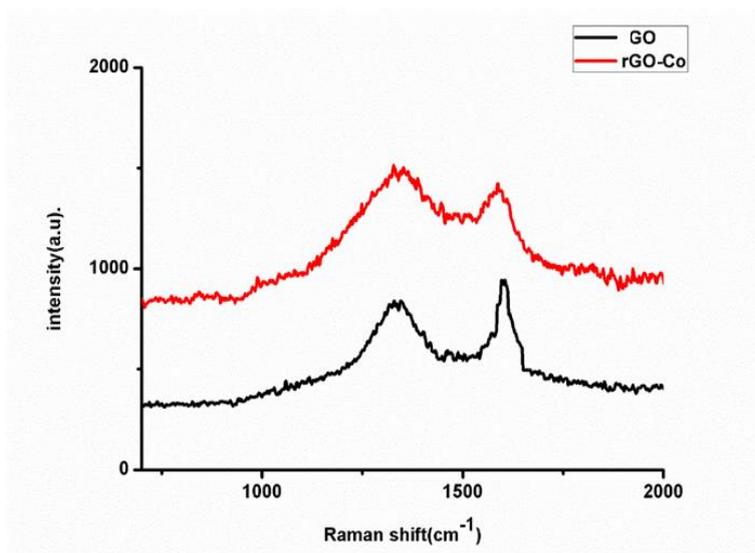




**Figure 1.** SEM images a) rGO, b) Co-rGO and c) EDS Elemental Mapping of Co

### 3.2 Raman spectroscopy

Raman spectroscopy is a valuable tool for obtaining information on the crystal structure and defects in graphene-based materials. The Raman spectra of GO and Co-rGO are displayed in Fig. 2, two distinct peaks can be observed. The peak centred at around  $1592\text{ cm}^{-1}$  is the G band which arises from the stretching of  $\text{sp}^2$  bonds in the carbon material. The peak at about  $1334\text{ cm}^{-1}$  is the D band which is due to the presence of defects in the graphitic lattice [20]. The ratio of D band intensity to G band intensity ( $I_D/I_G$ ) is a measure of the extent of disorder in carbon materials. The higher  $I_D/I_G$  of Co-rGO compared to GO is indicative of the *in situ* reduction of GO in the reaction for Co nanoparticles incorporation.. Expectedly, no peak can be attributed to Co nanoparticles in the Co-rGO spectrum.

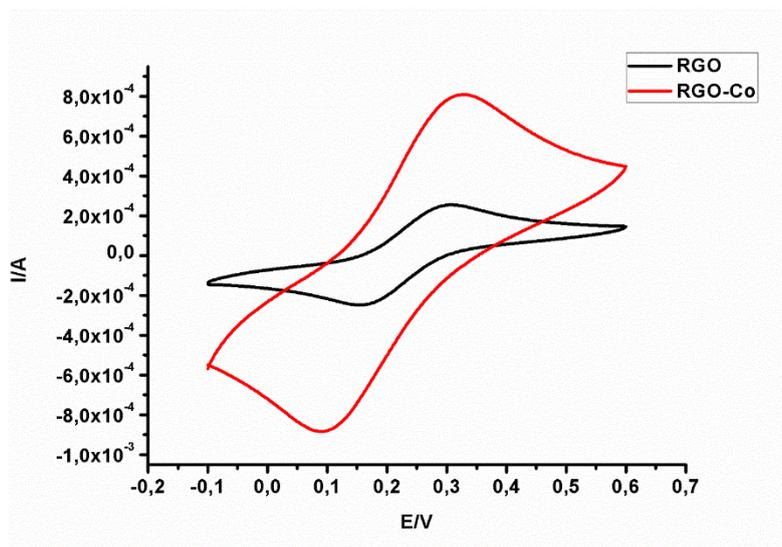


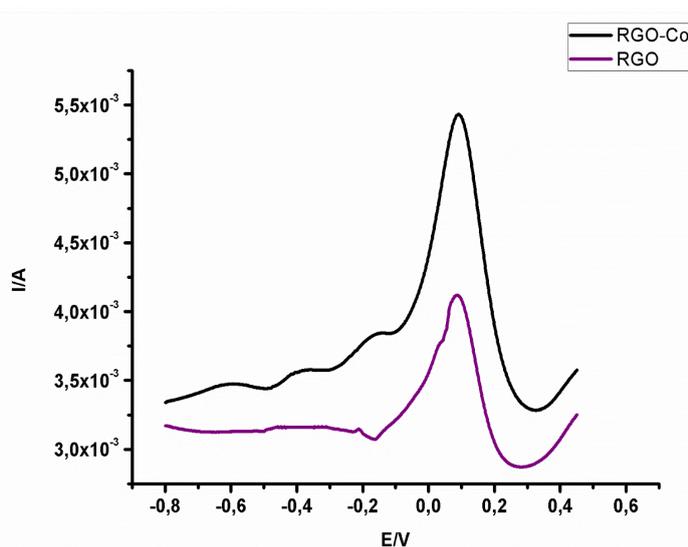
**Figure 2.** Raman spectra of GO and Co-rGO

### 3.3 Electrode characterization in redox probe and As(III)

The cyclic voltammograms (Fig. 3a) of rGO and Co-rGO modified EG electrodes were obtained in a 5 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  redox probe. The composite modifier gave rise to a higher peak current (also with a higher capacitive current) than the rGO modifier. This can be used as an indication of the incorporation of cobalt nanoparticles into the graphene sheets. The higher current can be attributed to the increase in the electroactive surface area which improved the sensitivity of the electrode. Scan rate studies (not shown) revealed that the peak current is directly proportional to the square root of the scan rate in the presence of 5 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  redox probe. The implied diffusion controlled kinetics supports the analytical application of the Co-rGO modified EG electrode.

Electrochemical detection of arsenic is based on the reduction of arsenic from  $\text{As}^{3+}$  to  $\text{As}^0$  [21]. In figure 3b, a reduction peak can be observed at 0.1 V which could be attributed to the transformation of  $\text{As}^{3+}$  to  $\text{As}^0$  at the surface of the electrode.





b)

**Figure 3.** Cyclic voltammograms of a) rGO and rGO-Co electrodes in 5 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  b) SWV at rGO and Co-rGO in As(III) solution

As observed with ferrocyanide redox probe, the current peak due to As reduction at Co-rGO modified EG electrode is much enhanced compared to that obtained at the rGO modified electrode. The cobalt nanoparticles increased the current response of the rGO for As reduction by over 50%, suggesting good electrocatalytic properties of the nanoparticles.

### 3.4 Optimisation of experimental parameters for As detection and quantification

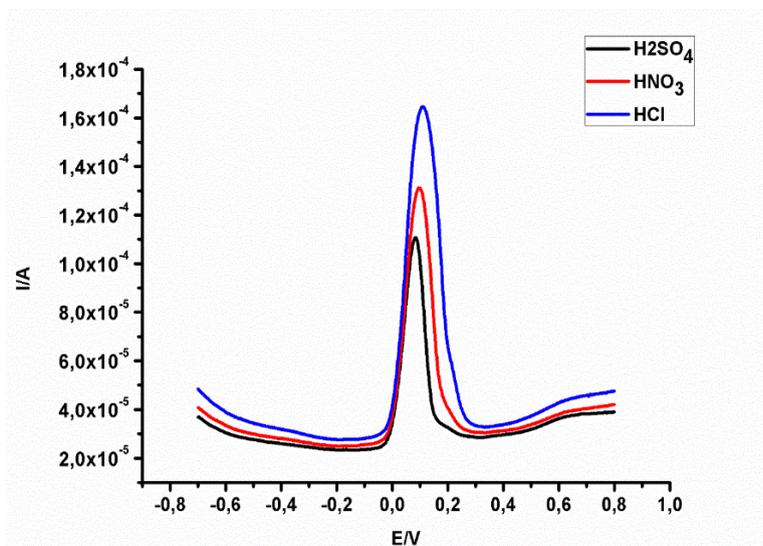
In order to obtain a maximum efficiency of the proposed method in the detection of As(III) ions in water, variables such as pH, scan rate, supporting electrolyte, deposition potential and deposition time need to be optimised.

#### 3.4.1 Effects of supporting electrolyte and pH on As detection

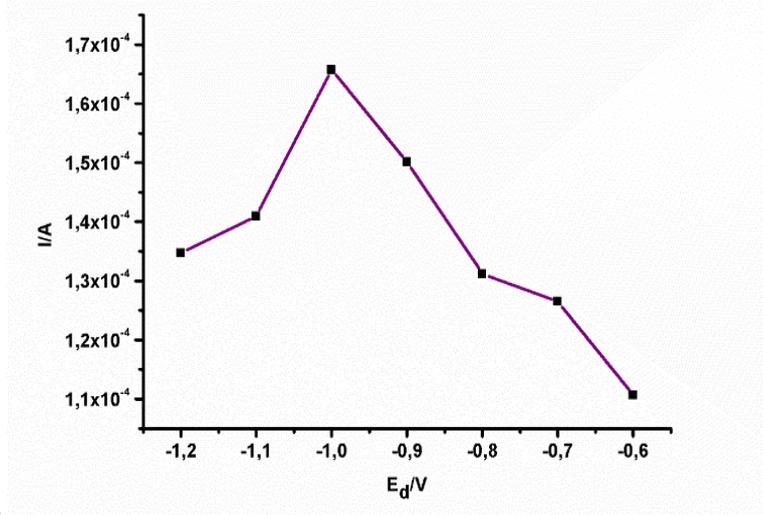
It has been reported that voltammetric detection of arsenic can be readily achieved in acidic media [22, 23]. As a result, three electrolytes, namely,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{HCl}$  were compared for As detection. The current peak observed when  $\text{HCl}$  was used was higher than that observed when either  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  was used (Fig. 4a) This result is consistent with earlier reports, and complexation of As to Cl ions has been suggested as possible reason for the improved current response obtained when  $\text{HCl}$  is used as a supporting electrolyte [22]. Consequently,  $\text{HCl}$  was chosen as the supporting electrolyte for As quantification in this work. An optimum pH of 1 (which gave the highest peak current) was chosen for  $\text{HCl}$ .

#### 3.4.2 Effects of deposition potential and deposition time

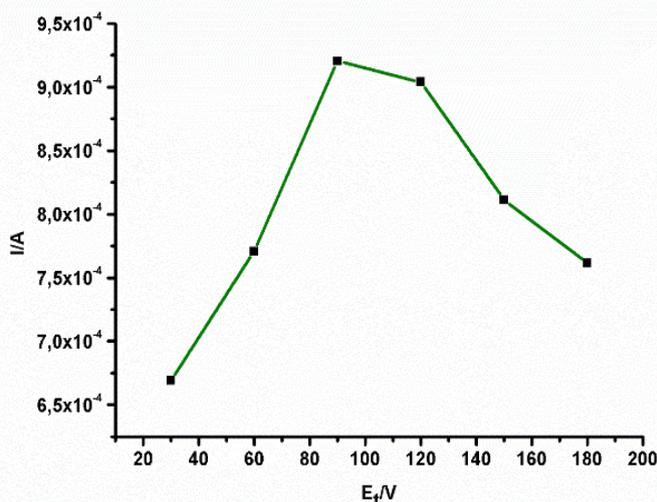
A potential range -0.6 to -1.2 V was selected to investigate the effect of potential on the deposition of As.



a)



b)



c)

**Figure 4.** a) SWV showing the effects of different supporting electrolytes on As detection at Co-rGO modified EG electrode. Plots of b) Current vs E, showing the effect of deposition potential detection, c) Current vs time, showing the effect of deposition, on As detection

The highest peak current was achieved at -1.0 V (Fig. 4b). This potential was then chosen as optimum and used in subsequent measurements. Deposition time is another important parameter that must be investigated in anodic stripping analysis of metal ions. The current response of As, for instance, is affected by how much time is taken for As(III) ions to accumulate from the bulk solution onto the surface of the electrode and how long they stay at the electrode. In this work, deposition time was varied from 30 s to 180 s, with the highest current response achieved at 90 s (Fig 4c).

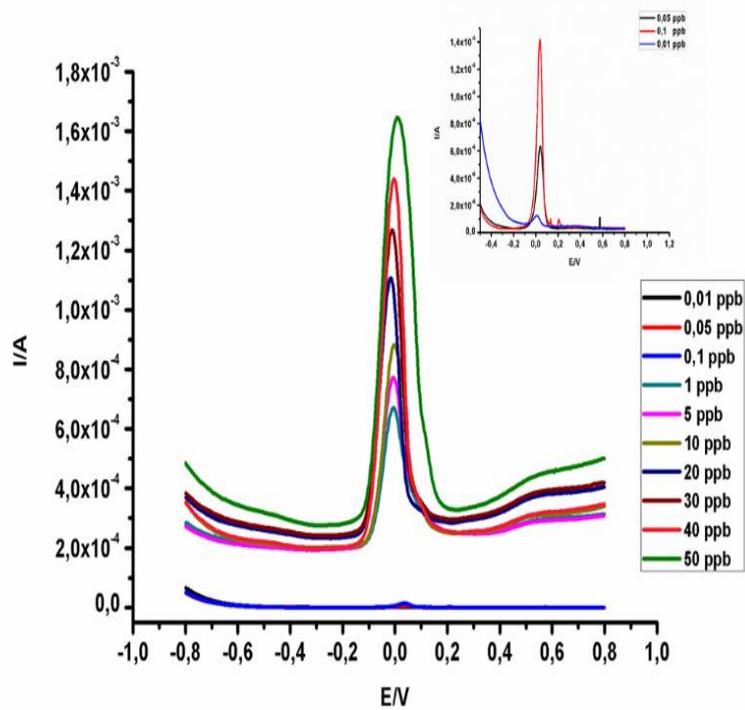
### 3.5 Detection of As(III) at Co-rGO modified EG electrode

Under the optimum conditions, the square wave anodic stripping voltamograms at a concentration range 1 - 50 ppb of As (III) ions is presented in Figure 5a with the corresponding calibration plot as Fig 5b. The peak currents varied linearly with As concentrations and the linear regression equation was  $y = 6.64608 \times 10^{-4} + 1.96169 \times 10^{-5}$  with a correlation coefficient of 0.9984. The detection limit calculated using  $3\sigma$  of blank/slope was 0.31ppb and the limit of quantification was 1.01ppb. It is significant to note that these values are much lower than the limit set by the WHO. Compared with some recent reports which dealt with voltammetric detection of As(III) in water (Table 1), this sensor presented an excellent performance.

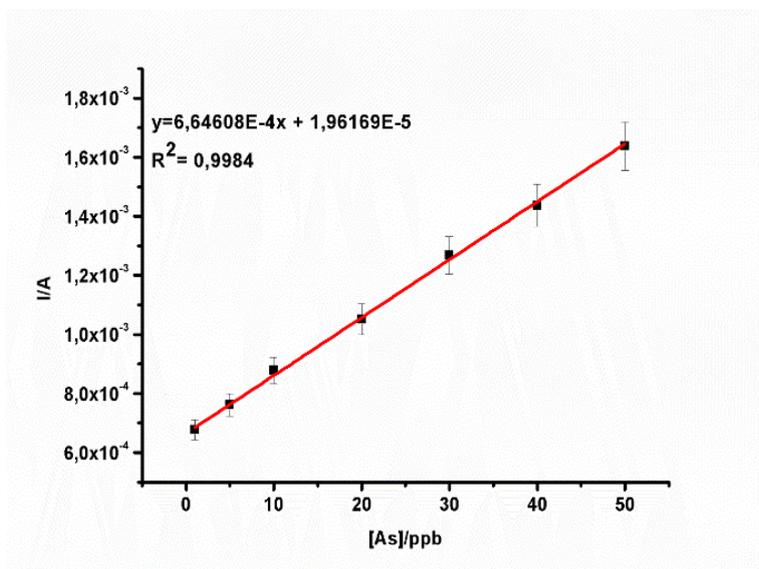
**Table 1.** Comparison of the performance of Co-rGO modified EG electrode with some reported electrodes

Electrode	Detection limit (ppb)	Reference
TTCA/rGO modified Au electrode	0.054	24

Au nanoparticles modified carbon fiber electrode	0.900	25
AuNPs/CeO <sub>2</sub> -ZrO <sub>2</sub> modified GCE	0.137	26
Porous Au modified GCE	0.490	27
Au nanoparticles modified GCE	0.180	28
[Ru(bpy) <sub>3</sub> ] <sup>2+</sup> -GO modified screen printed electrode	1.573	29
Co nanoparticles and rGO modified exfoliated graphite electrode	0.310	This work



a)



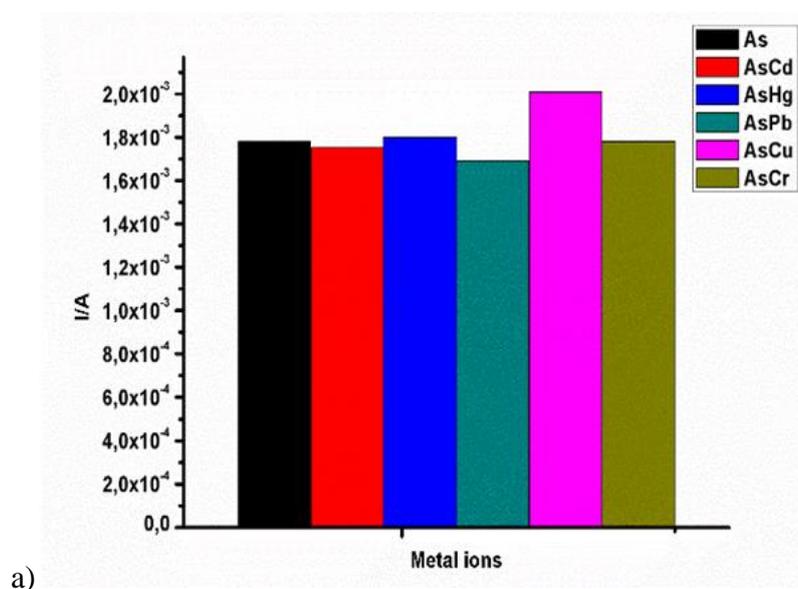
b)

**Figure 5.** a) Square wave anodic stripping voltamograms of various concentrations of As(III) (b) Calibration plot of peak currents vs As(III) concentrations.

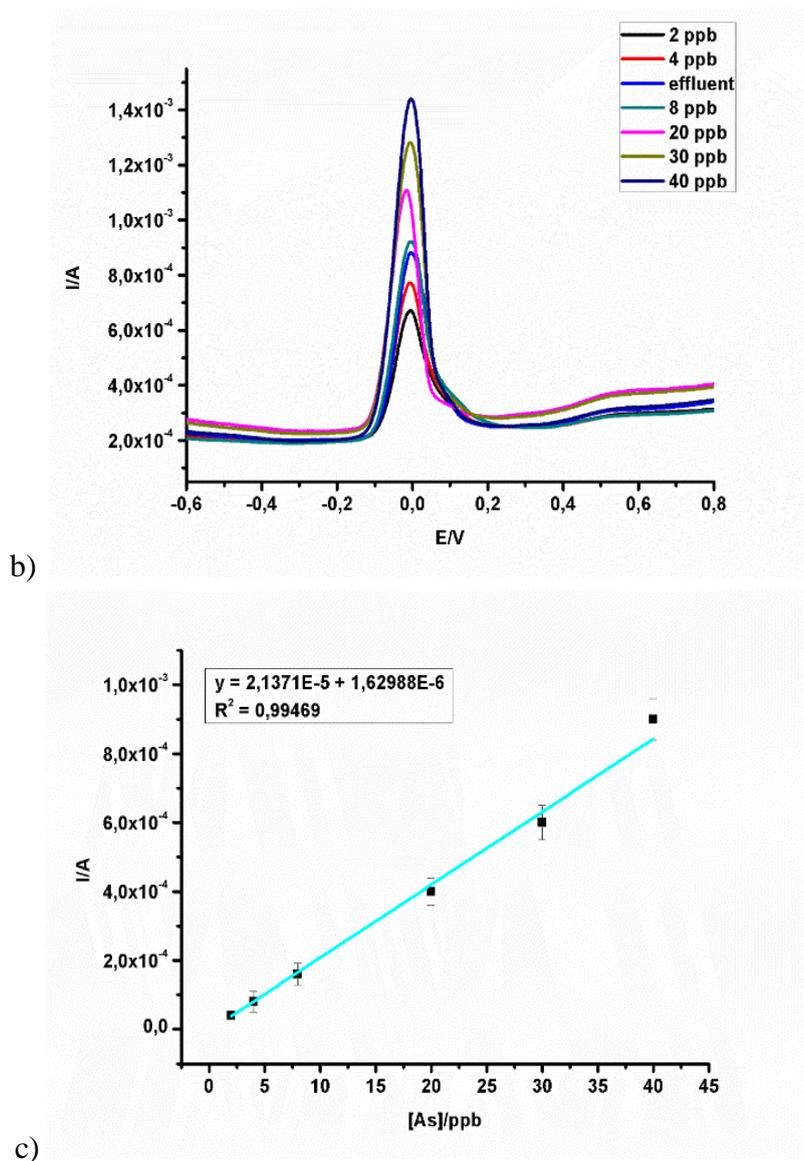
### 3.6 Reproducibility and repeatability study

The current responses of eight electrodes in 20 ppb As(III) ions were measured to investigate the reproducibility of the Co-rGO modified EG electrode. The RSD of the current values was found to be 5.44%, showing that the sensor is of analytical significance. For repeatability of the proposed method, eight measurements were done on 30 ppb As(III) ions and a value of 2.62% was calculated as the relative standard deviation (RSD).

### 3.7 Metal interference studies and real water samples analysis



a)



**Figure 6.** a) Chart of different interfering metals on the current peak of Arsenic; b) SWASVs of various concentrations of As(III) in real water and c) Calibration plot of peak current vs As(III) concentrations

Analysis of interferences in Fig 6 shows that the Co-rGO modified EG electrode sensor was not interference prone in the presence of common ions such as  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cr^{6+}$  and  $Pb^{2+}$  (Fig 6a). This is consistent with the earlier report by Mafa et al. [12].  $Cu^{2+}$  ions were the major interferences in the detection of Arsenic. Addition of  $Cu^{2+}$  ions to the solution of  $As^{3+}$  showed the highest interference of about 12% (Fig 6a), this is a significant increase in the peak current of As (Fig. 6a).

Real water sample was collected from a river in Pretoria, South Africa. Prior to analysis, the sample was filtered through a  $0.2 \mu m$  filter to remove any fine particles and was subsequently acidified with HCl to the optimum pH determined earlier. The concentration of As found in the water sample using the proposed sensor was  $9.35 \pm 0.25$  ppb (Fig 6b,c). The same water sample was analysed for As using ICP-OES and the concentration of Arsenic was found to be  $9.44 \pm 0.18$  ppb. A comparison of the

As concentrations detected in the real water sample by both the sensor and ICP-OES clearly shows that the sensor is suitable for quantification of As in real environmental samples.

**Table 2.** As(III) quantification in river water by this method and ICP-OES

	Concentration (ppb)
This sensor	9.35±0.25
ICP-OES	9.44±0.18

#### 4. CONCLUSION

In this study, cobalt nanoparticles were successfully incorporated onto the reduced graphene oxide sheets and the resulting composite material was used to modify exfoliated graphite electrode for detection of As (III) in water. The composite modifier enhanced the electrochemical response of the EG electrode towards As ions in water. At optimised experimental conditions, the sensor was employed for the quantification of the analyte in a water sample collected from a river in Pretoria, South Africa. From the outcome of this study and the versatility of EG electrodes in general, this sensor can be explored for practical analysis.

#### ACKNOWLEDGEMENTS

The authors would like to gratefully acknowledge the following South African bodies for financial supports: NRF DST-NRF Centre of Excellence in Strong Materials, Centre for Nanomaterials Science Research, University of Johannesburg and National Research Foundation of South Africa (CPRR Grant number: 98887).

#### References

1. S. Chowdhury, M.J. Mazumder, O. Al-Attas, T. Husain, *Science of the Total Environment* 569 (2016) 476-488.
2. A.E. Duncan, N. de Vries, K.B. Nyarko, *Environmental Nanotechnology, Monitoring & Management* (2018). <https://doi.org/10.1016/j.enmm.2018.06.003>.
3. B. Genthe, T. Kapwata, W. Le Roux, J. Chamier, C.Y. Wright, *Chemosphere* 199 (2018) 1-9.
4. S. Kapaj, H. Peterson, K. Liber, P. Bhattacharya, *Journal of Environmental Science and Health: Part A* 41 (2006) 2399-2428.
5. P. Mandal, *Emerging Contaminants* 3 (2017) 17-22.
6. Guidelines for drinking-water quality: fourth edition incorporating the first addendum. Geneva: World Health Organization; 2017. Licence: CC BY-NC-SA 3.0 IGO.
7. M.G. Peleyeju, A.O. Idris, E.H. Umukoro, J.O. Babalola, O.A. Arotiba, *ChemElectroChem* 4 (2017) 1074-1080.
8. G. Bhanjana, N. Mehta, G.R. Chaudhary, N. Dilbaghi, K.-H. Kim, S. Kumar, *Journal of Molecular Liquids* 264 (2018) 198-204.
9. P. Carrera, P.J. Espinoza-Montero, L. Fernández, H. Romero, J. Alvarado, *Talanta* 166 (2017) 198-206.

10. Y.-H. Yuan, X.-H. Zhu, S.-H. Wen, R.-P. Liang, L. Zhang, J.-D. Qiu, *Journal of Electroanalytical Chemistry* 814 (2018) 97-103.
11. R.C. Rodríguez, M.M. Bruno, P.C. Angelomé, *Sensors and Actuators B: Chemical* 254 (2018) 603-612.
12. P.J. Mafa, A.O. Idris, N. Mabuba, O.A. Arotiba, *Talanta* 153 (2016) 99-106.
13. T. Ndlovu, B.B. Mamba, S. Sampath, R.W. Krause, O.A. Arotiba, *Electrochimica Acta* 128 (2014) 48-53.
14. T. Ndlovu, O.A. Arotiba, B.B. Mamba, *Int. J. Electrochem. Sci.* 9 (2014) 8330-8339.
15. P. Ramesh, G. Suresh, S. Sampath, *Journal of Electroanalytical Chemistry* 561 (2004) 173-180.
16. M.G. Peleyeju, E.H. Umukoro, L. Tshwenya, R. Moutloali, J.O. Babalola, O.A. Arotiba, *RSC Advances* 7 (2017) 40571-40580.
17. M. Peleyeju, E. Umukoro, J. Babalola, O. Arotiba, *Electrocatalysis* 7 (2016) 132-139.
18. Z. Ji, X. Shen, Y. Song, G. Zhu, *Materials Science and Engineering: B* 176 (2011) 711-715.
19. X. Cui, R. Lv, R.U.R. Sagar, C. Liu, Z. Zhang, *Electrochimica Acta* 169 (2015) 342-350.
20. R.K. Kampara, P. Rai, B. Jeyaprakash, *Sensors and Actuators B: Chemical* 255 (2018) 1064-1071.
21. D.X.O. Jaramillo, A. Sukeri, L.P. Saravia, P.J. Espinoza-Montero, M. Bertotti, *Electroanalysis* 29 (2017) 2316-2322.
22. W.-W. Li, F.-Y. Kong, J.-Y. Wang, Z.-D. Chen, H.-L. Fang, W. Wang, *Electrochimica Acta* 157 (2015) 183-190.
23. F. Pereira, M. Vázquez, L. Debán, A. Aller, *Talanta* 152 (2016) 211-218.
24. Y.-H. Yuan, X.-H. Zhu, S.-H. Wen, R.-P. Liang, L. Zhang, J.-D. Qiu, *Journal of Electroanalytical Chemistry* 814 (2018) 97-103
25. P. Carrera, P.J. Espinoza-Montero, L. Fernández, H. Romero, R. Alvarado, *Talanta* 116 (2017) 198-206
26. M. Yang, P.-H. Li, W.-H. Xu, Y. Wei, L.-N. Li, Y.-Y. Huang, Y.-F. Sun, X. Chen, J.-H. Liu, X.-J. Huang, *Sensors and Actuators B: Chemical* 255 (2018) 226-234
27. L. Chao, X. Xiong, J. Liu, A. Xu, T. Huang, F. He, Q. Xie, *Sensors and Actuators B: Chemical* 253 (2017) 603-611
28. M.A. Kamyali, A. Aghaei, *Electrochimica Acta* 206 (2016) 192-198
29. M.B. Gumpu, M. Veerapandian, U.M. Krishnan, J.B.B. Rayappan, *Chemical Engineering Journal* 351 (2018) 319-327