Development of a Nanocomposite-Based Electrochemical Sensing of Arsenic in Aqueous Solution

Omer Sadak[1*]

[1] Department of Electrical and Electronics Engineering, Ardahan University, Ardahan, Turkiye
[*1] omersadak@ardahan.edu.tr

Abstract: Contamination of drinking water with heavy metals is a serious threat to the global environment and public health. Currently, approximately 20 countries have been reported for arsenic levels present in drinking water that are higher than the EPA guidelines. Arsenic is highly toxic, widely dispersed and found in the earth's crust. It can be found in inorganic as well as organic compounds in water. Arsenic is released into the environment in a variety of ways, including industrial effluents, pesticides, wood preservative chemicals, combustion of petroleum and coal, and mining operations. Currently, Arsenic is determined using a wide variety of methods that include inductively coupled plasma mass spectrometry (ICPMS), high-performance liquid chromatography (HPLC) with ICPMS and graphite furnace atomic absorption spectrometry (GFAAS). Nevertheless, these methods are slow, expensive and require skilled people to operate. Alternatively, electrochemical sensors have been potentially recognized as a powerful analytical method for the detection of heavy metals at very low concentrations. It also allows on-site and continuous monitoring of heavy metals. A nanocomposite consisting of gold nanoparticles and conducting polymers (polydiallyldimethylammonium chloride (PDDA) and polystyrene sulfonate (PSS)) functionalized graphene was used in this study to detect arsenic, which causes major environmental and health concerns.

Key words: Electrochemical Sensors, Arsenic, Heavy metals.

Sulu Çözeltide Arseniğin Nanokompozit Tabanlı Elektrokimyasal Algılanmasının Geliştirilmesi

Öz: İçme sularının ağır metallerle kirlenmesi, küresel çevre ve halk sağlığı için ciddi tehdit oluşturmaktadır. Şu anda yaklaşık 20 ülkede içme suyunda bulunan ve EPA yönergelerinden daha yüksek arsenik seviyeleri rapor edilmiştir. Arsenik oldukça zehirlidir, geniş çapta dağılmıştır ve yer kabuğunda bulunur. Suda hem organik hem de inorganik formda bulunur. Arseniğin çevreye salınım kaynakları, endüstriyel atıklar, pestisitler, odun koruyucu maddeler, fosil yakıtların yanması ve madencilik faaliyetleri yoluyla farklı şekillerde ortaya çıkmaktadır. Şu anda Arsenik, endüktif olarak eşleşmiş plazma kütle spektrometrisi (ICPMS), grafit fırınlı atomik absorpsiyon spektrometrisi (GFAAS) ve ICPMS'li yüksek performanslı sıvı kromatografisi (HPLC) dahil olmak üzere çok çeşitli yöntemler kullanılarak belirlenmektedir. Bununla birlikte, bu yöntemler yavaş, pahalıdır ve çalışması için yetenekli insanlar gerektirir. Alternatif olarak, elektrokimyasal sensörler, çok düşük konsantrasyonlarda ağır metallerin tespiti için potansiyel olarak güçlü bir analitik teknik olarak kabul edilmiştir. Ayrıca ağır metallerin yerinde ve sürekli olarak izlenmesine olanak tanır. Bu çalışmada, ciddi çevre ve sağlık sorunlarına neden olan Arsenik'in tespiti için altın nanopartikül ve iletken polimerlerden (polidiallildimetilamonyum klorür (PDDA) ve polistiren sülfonat (PSS)) işlevselleştirilmiş grafenden yapılmış bir nanokompozit kullanılmıştır.

Anahtar kelimeler: Elektrokimyasal Sensörler, Arsenik, Ağır metaller.

1. Introduction

Arsenic (As) contamination in drinking water is a worldwide problem. It is poisonous and the long-term exposure may cause serious toxicity and may lead to death [1]–[4]. As pollution in the environment takes place in a number of ways, including industrial effluents, wood preservative compounds, pesticides, burning of petroleum-based products, and mining operations. [5],[6]. Furthermore, the impacts of arsenic poisoning extend beyond human health to the ecosystem, affecting aquatic life and soil quality. Therefore, detection of As is crucial and currently, As^{3+} is determined using a wide variety of methods that include ICPMS, HPLC with ICPMS and GFAAS. However, these instruments are bulky, costly to run and maintain, and in addition, they require well-equipped laboratories and hence are only available for in-field detection of heavy metals [5],[7]–[9].

In contrast, electrochemical method has been potentially recognized as a powerful analytical technique for the detection of heavy metals at their lowest concentration in environmental samples due to its remarkable sensitivity [10]–[12]. There are a variety of electrochemical methods that can be employed for the detection of heavy metals. Among them, differential pulse anodic stripping voltammetry (DPASV) is commonly utilized for the detection of As. It is very robust, sensitive, productive, less expensive and portable for on-site analysis [13],[14]. This DPASV technique for the measurement of As^{3+} consists of electrochemical deposition of arsenic

---

on an electrode surface for a few seconds, followed by reverse potential scan oxidation of the metal back into solution. As a function of scan potential, the oxidation current, also known as stripping current, is recorded. [15]–[17]. The analytical signal is the resulting from peak-shaped (bell-shaped) voltammogram. DPASV is a two-fold process which first does the deposition of dropped arsenic concentration solution on the working surface before it is stripped [18],[19]. Optimizing DPASV for arsenic detection using a handheld device will reduce cost, allow on-site water analysis, and help initiate a rapid containment response in cases of highly contaminated water sources.

This study focuses on the utilization of a screen-printed carbon electrode (SPE) as the foundation for developing an electrochemical sensor. The working electrode surface of the SPE was modified through a stepwise process involving the incorporation of partially oxidized graphene (po-Gr), followed by the layered assembly of gold nanoparticles (AuNPs), polydiallyldimethylammonium chloride (PDDA), and polystyrene sulfonate (PSS). This tailored modification strategy aimed to enhance the sensor's performance and sensitivity in detecting arsenic ions As^{3+}. Remarkably, the fabricated electrochemical sensor exhibited a linear response in relation to As^{3+} concentration within the detection range of up to 1200 nM. This wide linear range indicates the sensor's capacity to accurately detect and quantify varying levels of As^{3+} ions, showcasing its potential applicability for monitoring arsenic contamination in drinking water sources. The successful integration of graphene, AuNPs, and the polymeric layers onto the SPE platform holds promise for advancing the field of electrochemical sensing, particularly in the context of heavy metal detection and environmental monitoring. The combination of the tailored electrode modification approach and the inherent electrochemical properties of the SPE contributes to the sensor's enhanced sensitivity, selectivity, and reliability, further emphasizing its potential as a cost-effective and efficient solution for the detection of heavy metal contaminants in water samples.

2. Materials and Methods

2.1. Reagents

CH Instruments, Inc. (Bee Cave, TX, USA) supplied the screen printed carbon electrodes (SPE) (TE100). Sigma Aldrich supplied the graphite flakes (150 m). ACROS Organics provided the hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4.3H_2O$), hydrochloric acid (76%), sodium hydroxide, and polydiallylydiammonium chloride (PDDA-20% w/w). The arsenic trioxide (As_2O_3) was obtained from Sigma Aldrich. All other reagents were obtained at the highest grade available from Sigma Aldrich or Fisher Scientific and were used without additional purification. All solutions were made with deionized (DI) water at room temperature with a resistivity of 18.2 M.cm (Ultrapure Water System, Millipore, Billerica, MA, USA).

2.2. Synthesis of AuNPs and po-Gr

Turkevich method was used to synthesize AuNPs [20]. Briefly, 2 mL of 10 mM $HAuCl_4.3H_2O$ was mixed with 18 mL DI H_2O. After the solution was boiled, 2mL of 1% sodium citrate was added to the boiling $HAuCl_4$ solution. The color was turned to dark brown solution and then turned to clear red/purple color.

The po-Gr was prepared as reported in our previous papers with some modification [21],[22]. Briefly, highly pure graphite electrodes were used as anode and cathode using 0.1 M potassium phosphate buffer solution at pH 7 at room temperature as an electrolyte solution. 3 V were applied for 1 h to electrochemically exfoliate graphite electrodes. Then obtained solution was filtered and re-dispersed into DI water. After ultra-sonication for 1h, the solution was collected for further use and concentration of po-Gr was set to 1 mg/ml.

2.3. Functionalization of SPE surface

SPE was functionalized using po-Gr, AuNPs and PDDS-PSS solution as illustrated in Figure 1. First the SPE electrode was immersed in DI water avoiding any air bubbles for 2 minutes and then was allowed to partially dry at room temperature. Firstly, 3 μl of 1 mg/ml of po-Gr was very carefully spiked on the working electrode surface without the pipette tip touching the working surface as it can damage the electrode. Next step was addition of AuNPs prepared by aqueous reduction of $HAuCl_4$ by sodium citrate, which was then followed by the addition of conductive polymers where, 2 μl of freshly prepared PDDA and PSS mixture (1:1 ratio) was spiked on to the working surface of electrode. Addition of each step is done at room temperature and each step takes approximately 30 min to dry.
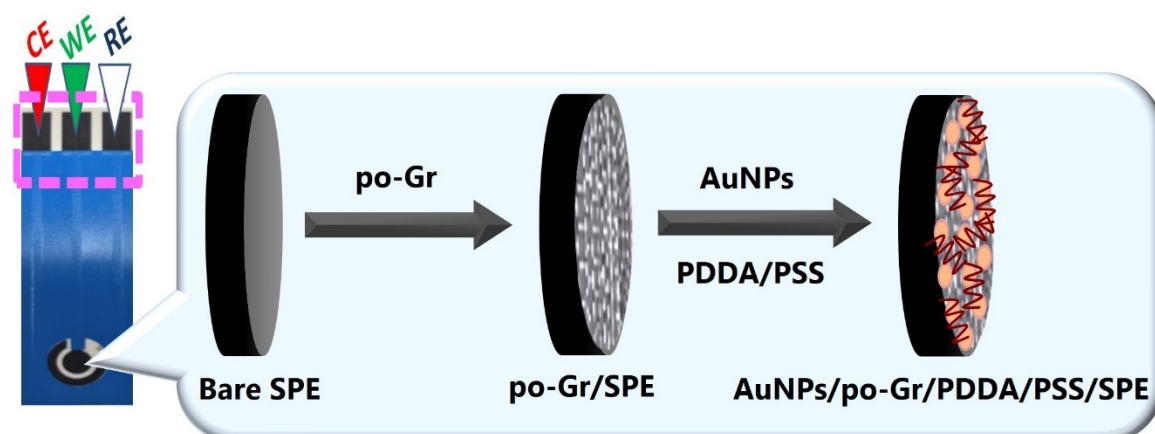
Figure 1. Schematic illustration of SPE preparation.

2.4. Electrochemical Measurements

For electrochemical measurements, an electrochemical workstation (660 D, CH Instruments) was employed. The electrochemical measurements consist of 2 steps as shown Figure 2, deposition and stripping. For the deposition step, analyte of interest (arsenic) is spiked onto the electrolyte solution (0.1 M PBS at pH 6). In the deposition step, As^{3+} is electrochemically reduced to As at -1.4V for 600 s. The As is deposited as a thin layer on the working surface of SPE. Next, a differential pulse anodic stripping voltammetry (DPASV) was utilized and As is oxidized to As^{3+}. This reduction and oxidation steps were repeated for various As concentration to obtain a linear fit. The redox reactions taking place during deposition and stripping are summarized below:

Step 1: Deposition
$$As^{3+} + 3e^- \rightarrow As \tag{1}$$
Step 2: Stripping
$$As \rightarrow As^{3+} + 3e^- \tag{2}$$
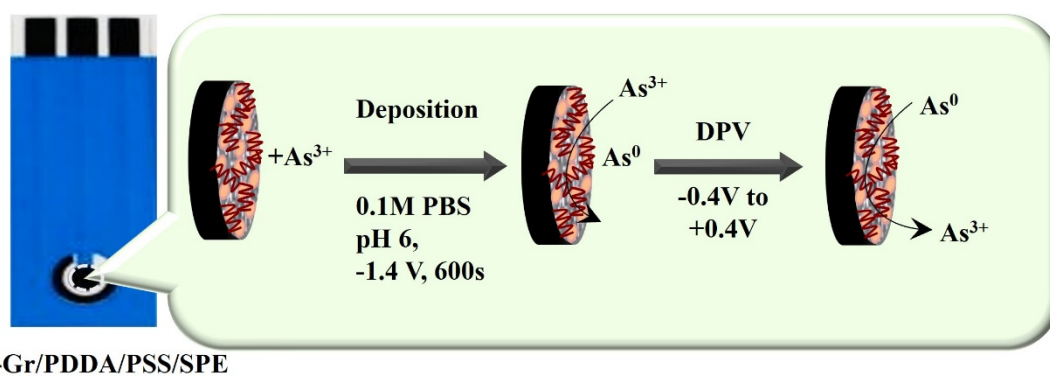

AuNPs/po-Gr/PDDA/PSS/SPE

Figure 2. Illustration of electrochemical sensing of As3+ using functionalized SPE electrode

2.5. Characterization

A scanning electron microscope (FE-SEM) (LEO1530, Carl Zeiss, Germany) was used to study surface morphology and 5 kV working voltage and 4 mm of working distance were used during testing. FEI Tecnai TF30 (Netherlands) were employed to collect transmission electron microscopy (TEM) images. For each sample, one drop of solution was placed on a carbon-coated 400 mesh copper grid, and excess solution was removed with filter paper. The grid was let to dry at ambient temperature before being imagined.

3. Results and Discussions

Figure 3a displays the FT-IR spectra of the synthesized pO-Gr and the pristine graphite sheet. The pristine graphite sheet does not exhibit any significant peaks, while the pO-Gr shows distinct peaks at approximately 3430, 2326, 1725, and 1642 cm^{-1}. These peaks correspond to the stretching vibrations of OH, CO2, C=O, and C=C bonds, respectively.

In Figure 3b, the Raman spectra of pO-Gr and the pristine graphite sheet are presented. The Raman spectrum of the pristine graphite sheet shows a small D band at 1353 cm^{-1}, indicating structural defects. It also displays a prominent G band at 1593 cm^{-1}, which is associated with the vibration of sp^2 hybridized carbon atoms in the n-plane, along with a 2D band at 2739 cm^{-1} corresponding to two phonon lattice vibrations. On the other hand, the pO-Gr exhibits significant D, G, and 2D bands at 1343, 1587, and 2687 cm^{-1}, respectively. These observations suggest the presence of localized sp^3 defects on the surface of the graphene sheets after exfoliation.
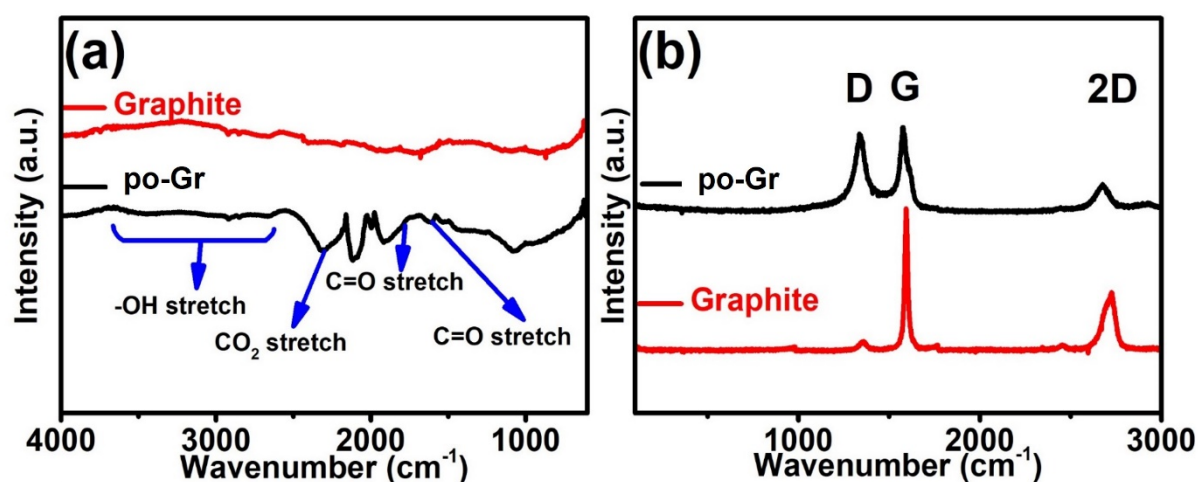

Figure 3. FT-IR and Raman spectra of po-Gr and pristine graphite

After the synthesis of po-Gr, AuNPs were synthesized using the Turkevich method as described above. The determination of both the size and concentration of spherical AuNPs can be achieved directly through analysis of UV−vis spectra. Figure 4 illustrates the UV spectra of AuNPs, demonstrating a pronounced absorption peak at 520 nm, indicating the presence of AuNPs with a particle size ranging from approximately 13 to 15 nm. Additionally, the TEM images of the AuNPs, depicted in Figure 5a, provide further visual confirmation of the formation of AuNPs and their size. Furthermore, particle size analysis of the AuNPs using a particle size analyzer, as shown in the inset of Figure 4, supports the successful formation of ~15 nm AuNPs.

The morphology of po-Gr and AuNPs-decorated po-Gr was analyzed using TEM, as depicted in Figure 5. Examination of po-Gr revealed its characteristic rippled and wrinkled morphology, as shown in Figure 5b. Upon treatment with AuNPs, the po-Gr surface exhibited well-dispersed AuNPs, as illustrated in Figure 5c and 5d. The TEM images clearly demonstrate the presence of AuNPs ranging in size from 10 to 20 nm on the po-Gr surface. This indicates successful deposition and dispersion of AuNPs onto the graphene material [23]. The decorated po-Gr structure with uniformly distributed AuNPs holds significant promise for enhancing the sensing performance and selectivity in the detection of arsenic. The combination of the unique properties of po-Gr and the catalytic activity of AuNPs offers potential advantages in the development of highly efficient electrochemical sensors for heavy metal detection, specifically arsenic, in drinking water. The TEM analyses provide valuable insights into the structural characteristics and morphology of the nanocomposite, validating its potential for effective arsenic detection and suggesting its applicability in addressing environmental and health concerns associated with heavy metal contamination in water sources.
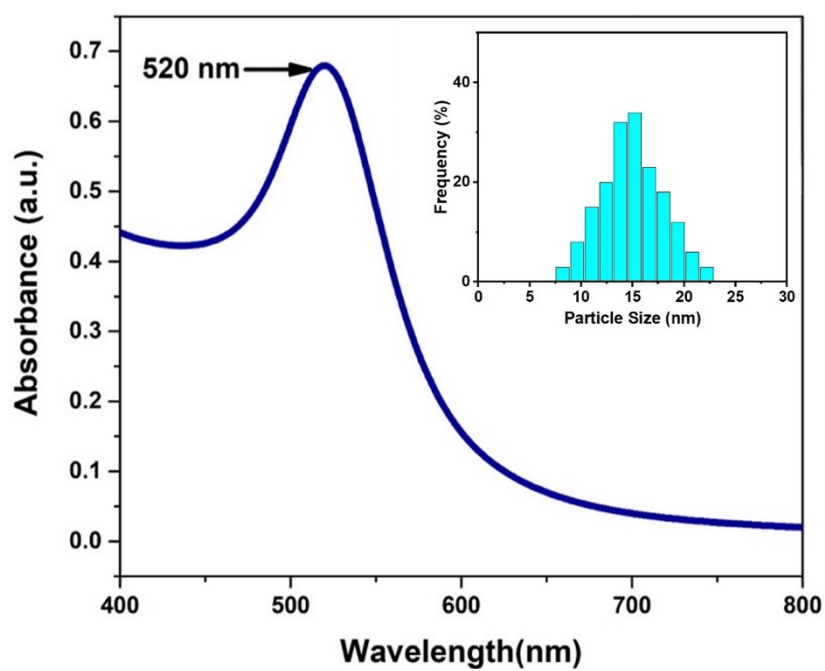
Figure 4. UV spectra of as-synthesized AuNPs. The inset is the particle size distribution of the AuNPs.
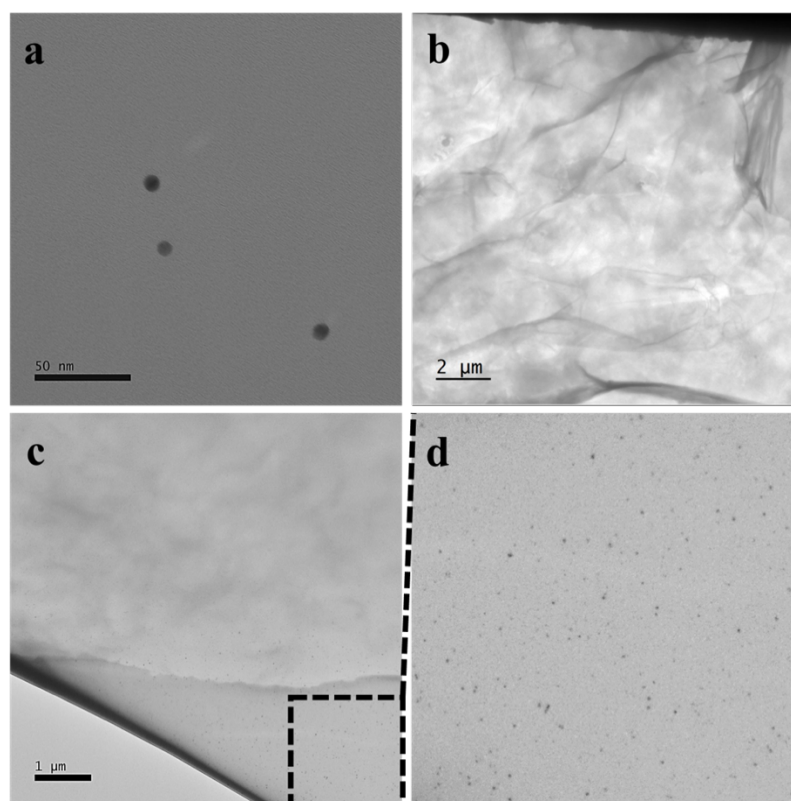

Figure 5. TEM images of (a) AuNPs, (b) po-Gr flake and (c) AuNPs decorated po-Gr flakes. (d) the enlarged view from AuNPs decorated po-Gr flake image.

To examine the surface characteristics of the SPE electrodes, a detailed analysis was performed using FE-SEM. The FE-SEM images provided valuable insights into the morphological features of the electrode surfaces. Figure 6a illustrates the surface morphology of the SPE electrode coated with po-Gr, revealing the distinctive rippled and wrinkled appearance that is characteristic of graphene materials. Subsequently, additional layers were sequentially added onto the po-Gr-coated SPE electrode, including AuNPs, PDDA, and PSS. The FE-SEM image of the AuNPs/po-Gr/PDDA/PSS-coated SPE electrode demonstrated the successful formation of a well-dispersed nanocomposite, as depicted in Figure 6b. The nanocomposite layer exhibited a uniform distribution of AuNPs on the po-Gr surface, further validating the effective fabrication process and the compatibility of the components within the sensor design.
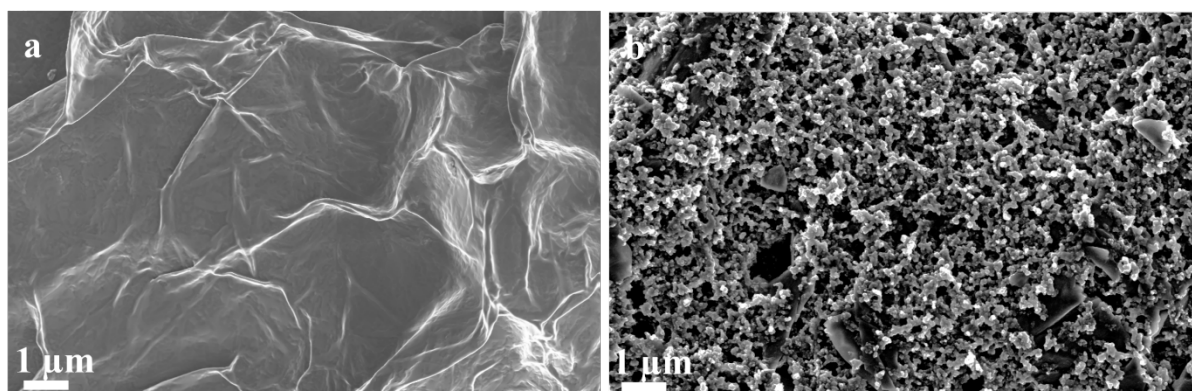

Figure 6. SEM images of (a) po-Gr and (b) AuNPs/po-Gr/PDDA/PSS coated SPE electrode.

Then, the SPE electrode was tested using DPASV method. This analytical technique consists of 2 steps as shown in Figure 2, deposition and stripping. For the deposition step, analyte of interest (arsenic) is spiked on the working surface of the electrode and the supporting electrolyte used is PBS at pH 6 (slightly acidic by addition of HCl). In the deposition step, As^{3+} is electrochemically reduced to As at a sufficiently negative potential (-1.4V) for 600s. The As is deposited as a thin layer on the surface of working electrode. A linearly increasing voltage is provided to the sensor during the electrochemical sensing process, causing As to be oxidized and converted to As^{3+}, resulting in the formation of an anodic current. This current response is recorded for further analysis. To assess the sensitivity and linear range of the sensor, the responses obtained from the DPASV experiments are presented in Figure 7a. The findings indicate that the current peak observed at -0.32 V exhibits an increasing trend as the concentrations of the As^{3+} stock solution is raised.
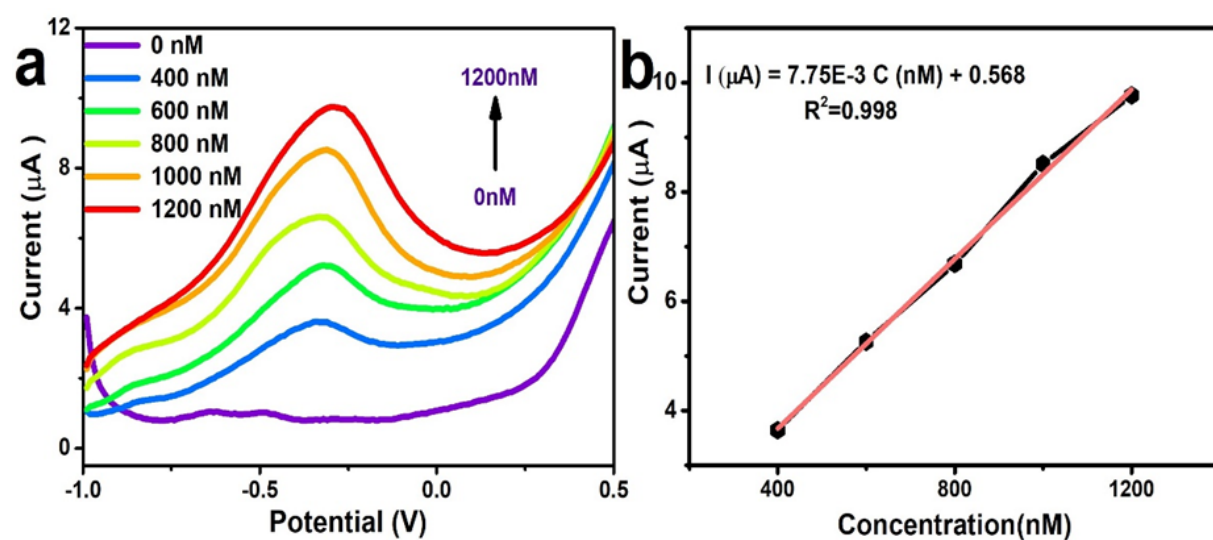

Figure 7. (a) DPASV curves for As^{3+} detection and (b) its linear curve fit
Furthermore, a calibration plot for As^{3+} is constructed by correlating the current peak height with each corresponding concentration. Remarkably, the calibration curve (Figure 7b) exhibits linearity within the

concentration range of 0-1200 nM, as demonstrated by the linear regression equation: I(μA) = 7.75E-3 C (nM) + 0.568 (R^2 = 0.998). This equation signifies a sensitivity of 86.18 μA/nM, as depicted in Figure 7b. The results highlight the excellent performance of the sensor in accurately detecting and quantifying varying concentrations of As^{3+} through its electrochemical response.

For the arsenic detection application in this study, the use of a nanocomposite formulation containing conducting polymers (PDDA, and PSS), po-Gr and AuNPs is well-justified. The chosen nanocomposite provides a promising solution to the widespread problem of arsenic contamination in drinking water by utilizing the catalytic properties of AuNPs, the stability and conductivity enhancement of conducting polymers, and the exceptional electrical properties of partially oxidized graphene po-Gr [4],[24]. A screen-printed carbon electrode (SPE) was subjected to a stepwise functionalization process, and the resulting sensor exhibits a broad linear response range for As^{3+}, offering a precise, quick, and affordable solution for addressing arsenic pollution in drinking water sources.

The detection limit attained in this work utilizing the proposed nanocomposite-based electrochemical sensor is relevant and compares favorably to the existing literature on arsenic detection methods. The sensor's sensitivity falls within a range that is appropriate for practical applications, as shown by the linear calibration curve's detection limit of up to 1200 nM. The achieved detection limit of 1200 nM enables the identification of arsenic concentrations that significantly exceed the permissible arsenic concentration levels in drinking water as set by the World Health Organization (WHO) guidelines (10 μg/L, equivalent to 133.3 nM) [25]. This suggests that the sensor can detect low quantities of arsenic that could be harmful to human health even when they are present in water sources. An important tool for real-world applications, particularly in areas where exposure to arsenic is a serious concern, is the sensor's ability to detect arsenic at such levels in combination with its portability and on-site monitoring capabilities. As a result, the achieved detection range is not only valuable but also extremely pertinent for real-world environmental and health applications.

4. Conclusions

The SPE electrode was utilized for the fabrication of the sensor by drop-casting the nanocomposite onto its surface employing a layer-by-layer method. Through comprehensive analytical investigations, it was observed that the developed sensor exhibited remarkable detection capability for As^{3+} ions, with a detection limit of up to 1200 nM. This detection limit places the sensor in a highly competitive position when compared to other existing electrochemical sensors. Notably, the proposed sensor offers significant advantages in terms of time and cost efficiency. The utilization of disposable SPEs eliminates concerns regarding surface fouling and electrode saturation, thereby ensuring consistent and reliable performance. Moreover, the unique design and composition of the sensor allow for convenient in situ measurements, enabling real-time monitoring and detection of As^{3+} levels in diverse settings. Overall, the incorporation of the nanocomposite onto the SPE electrode presents a promising approach for the development of a cost-effective, efficient, and portable electrochemical sensor for the detection of heavy metals, particularly As, in drinking water. This advancement holds considerable potential for addressing the pressing environmental and public health challenges associated with heavy metal contamination in water sources worldwide.

Acknowledgments

References

[1] Chakraborti D, Rahman MM, Mukherjee A, et al. Groundwater arsenic contamination in Bangladesh-21 Years of research. *J Trace Elem Med Biol*. 2015;31:237-248.
[2] Fisher AT, López-Carrillo L, Gamboa-Loira B, Cebrián ME. Standards for arsenic in drinking water: Implications for policy in Mexico. *J Public Health Policy*. 2017;38(4):395-406.
[3] Assirelli A, Ieffa S, Bernasconi R, Nobili L, Magagnin L. Graphene Based Materials for Arsenic Sensing and Removal from Contaminated Water. *ECS Meet Abstr*. 2015;MA2015-01(40):2127-2127.
[4] Udayan APM, Kachwala B, Karthikeyan KG, Gunasekaran S. Ultrathin quasi-hexagonal gold nanostructures for sensing arsenic in tap water. *RSC Adv*. 2020;10(34):20211-20221.
[5] Colliver TL, Ewing AG. Neurotransmitters, Electrochemical Detection of. *Encycl Anal Chem*. 2000:1-25.
[6] Wuana RA, Okieimen FE. Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. *ISRN Ecol*. 2011;2011:1-20.
[7] Dai X, Nekraseova O, Hyde ME, Compton RG. Anodic stripping voltammetry of arsenic(III) using gold nanoparticle-modified electrodes. *Anal Chem*. 2004;76(19):5924-5929.

[8] Domínguez-González R, González Varela L, Bermejo-Barrera P. Functionalized gold nanoparticles for the detection of arsenic in water. *Talanta*. 2014;118:262-269.

[9] Toor SK, Devi P, Bansod BKS. Electrochemical Detection of Trace Amount of Arsenic (III) at Glassy Carbon Electrode Modified with Au/Fe3O4 Nanocomposites. *Aquat Procedia*. 2015;4:1107-1113.

[10] Piech R, Kubiak WW. Determination of trace arsenic with DDTC-Na by cathodic stripping voltammetry in presence of copper ions. *J Electroanal Chem*. 2007;599(1):59-64.

[11] Profumo A, Merli D, Pesavento M. Voltammetric determination of inorganic As(III) and total inorganic As in natural waters. *Anal Chim Acta*. 2005;539(1-2):245-250.

[12] Rao Y, Li RH, Zhang DQ. A drug from poison: How the therapeutic effect of arsenic trioxide on acute promyelocytic leukemia was discovered. *Sci China Life Sci*. 2013;56(6):495-502.

[13] Forsberg G, O'Laughlin JW, Megargle RG, Koirtyohann SR. Determination of Arsenic by Anodic Stripping Voltammetry and Differential Pulse Anodic Stripping Voltammetry. *Anal Chem*. 1975;47(9):1586-1592.

[14] Kato D, Kamata T, Kato D, Yanagisawa H, Niwa O. Au Nanoparticle-Embedded Carbon Films for Electrochemical As3+ Detection with High Sensitivity and Stability. *Anal Chem*. 2016;88(5):2944-2951.

[15] Cinti S, Politi S, Moscone D, Palleschi G, Arduini F. Stripping Analysis of As(III) by means of screen-printed electrodes modified with gold nanoparticles and carbon black nanocomposite. *Electroanalysis*. 2014;26(5):931-939.

[16] Laschi S, Bagni G, Palchetti I, Mascini M. As(III) voltammetric detection by means of disposable screen-printed gold electrochemical sensors. *Anal Lett*. 2007;40(16):3002-3013.

[17] Niu X, Lan M, Zhao H, Chen C, Li Y, Zhu X. Review: Electrochemical Stripping Analysis of Trace Heavy Metals Using Screen-Printed Electrodes. *Anal Lett*. 2013;46(16):2479-2502.

[18] Li C. Determination of Arsenic in Water by Potentially Portable Methodology. 2013.

[19] Mays DE, Hussam A. Voltammetric methods for determination and speciation of inorganic arsenic in the environment-A review. *Anal Chim Acta*. 2009;646(1-2):6-16.

[20] Nadeau JL. Synthesis of Gold Nanoparticles /. *Introd to Exp Biophys - A Lab Guid*. 2020:154-159.

[21] Sadak O, Sundramoorthy AK, Gunasekaran S. Highly selective colorimetric and electrochemical sensing of iron (III) using Nile red functionalized graphene film. *Biosens Bioelectron*. 2017;89:430-436.

[22] Sadak O, Sundramoorthy AK, Gunasekaran S. Facile and green synthesis of highly conductive graphene paper. *Carbon N Y*. 2018;138:108-117.

[23] Sadak O. One-pot scalable synthesis of rGO/AuNPs nanocomposite and its application in enzymatic glucose biosensor. *Nanocomposites*. 2021;7(1):44-52.

[24] Sadak O, Wang W, Guan J, Sundramoorthy AK, Gunasekaran S. MnO2 Nanoflowers Deposited on Graphene Paper as Electrode Materials for Supercapacitors. *ACS Appl Nano Mater*. 2019;2(12):4386-4394.

[25] Ahn J, Boroje IJ, Ferdosi H, Kramer ZJ, Lamm SH. Prostate cancer incidence in U.S. counties and low levels of arsenic in drinking water. *Int J Environ Res Public Health*. 2020;17(3).