

Fabrication of a “Green” and Low–Cost Screen–Printed Graphene Sensor and Its Application to the Determination of Caffeine by Adsorptive Stripping Voltammetry

Nikolitsa Lezi¹, Solon Economopoulos², Mamantos Prodromidis³, Anastasios Economou^{1,*}, Nikos Tagmatarchis²

¹Laboratory of Analytical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Athens, 157 71, Greece

²Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, 116 35 Athens, Greece

³Laboratory of Analytical Chemistry, Department of Chemistry, University of Ioannina, Ioannina 45110, Greece

*E-mail: aeconomou@chem.uoa.gr

Received: 23 March 2017 / *Accepted:* 25 April 2017 / *Published:* 12 June 2017

This work reports the development of low–cost graphene–based screen–printed sensors using a “green” fabrication procedure. Three–electrode sensors featuring carbon working and counter electrodes and a Ag reference electrode were fabricated by screen–printing on flexible polymer film. Graphene suspension was prepared following a simple, fast and environment–friendly method of solvent exfoliation of graphite in N–methyl pyrrolidone (NMP). Graphene was further dispersed in Nafion and the solution was used to drop–coat the working electrode of the sensor. The modified electrode was characterized using Raman spectroscopy, scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS). The graphene/Nafion modified sensors were used to determine caffeine by anodic adsorptive stripping voltammetry. The procedure consists of a short adsorptive preconcentration step of caffeine on the graphene working electrode followed by an anodic voltammetric scan in the differential pulse (DP) mode. The oxidation current of caffeine is related to its concentration in the sample. High sensitivity was achieved due to the preconcentration step of the target compound on the working electrode. The limit of detection (LOD) for caffeine was 0.021 $\mu\text{mol L}^{-1}$ and the % relative standard deviation ($n=8$) was 2.0 %. The sensors were applied to the determination of caffeine in coffee and beverage samples.

Keywords: caffeine; graphene; Nafion; adsorptive stripping voltammetry; coffee; beverages

1. INTRODUCTION

Caffeine (1,3,7–trimethylxanthine, CAF) is a xanthine alkaloid that acts as a natural stimulant of the central nervous system. Owing to its distinct flavor and powerful psychoactive effects, caffeine

is the most widely used stimulant and its economic importance cannot be overemphasized. It is found in coffee and tea, it is widely used as an additive in drinks and beverages and is an ingredient of over-the-counter medications [1,2]. However, voluntary or involuntary overdose of caffeine can induce adverse side effects to consumers such as oversensitivity, irritability, anxiety, insomnia, etc [1,2]; therefore reliable analytical methods are required for its determination in food samples. Chromatographic and spectroscopic methods have been widely used for this purpose [3, 4]. Electrochemical methods have also been used for caffeine determination since they provide some advantages in terms of operational and instrumental simplicity, sensitivity, linear range, running and capital cost, rapidity and potential for miniaturization. In particular, the voltammetric determination of caffeine is based on its oxidation signal, usually in acidic medium to avoid oxidation of the supporting electrolyte [5].

Graphene is the thinnest and lightest sp² carbon nanomaterial consisting of a one-atom-thick planar sheet of sp²-bonded carbon atoms in a honeycomb crystal lattice and possesses extraordinary properties: excellent thermal and electrical conductivity, large surface area, fast heterogeneous electron transfer rates and high mechanical strength. Among its many other uses, graphene has been extensively used for the fabrication of chemical sensors and biosensors [6-9].

The various methods for the synthesis of graphene have been reviewed extensively [10,11]. For electrochemical sensing, only small quantities of graphene are necessary, therefore top-down synthetical approaches (involving breaking apart the stacked layers of graphite to yield single graphene sheets) are generally preferable in terms of cost, simplicity and purity of the final material to bottom-up methods (involving synthesizing graphene from alternative carbon-containing sources) [10].

Over the last few years, a handful of graphene-modified electrodes have been developed for the voltammetric determination of caffeine (Table 1). Yet, the majority of these are based on graphene prepared via chemical reduction or electroreduction of graphene oxide [12-19]. The major drawback of graphene oxide for graphene production is that it contains many defects in the sp² carbon lattice induced during the oxidation process and is electrically insulating. Subsequent reduction of graphene oxide does not effectively restore these defects in the sp² carbon lattice or the conductivity, thus the unique electronic properties of graphene are degraded. In addition, this method also involves the use of strongly oxidizing and reducing reagents, causing safety concerns and environmental issues and is time-consuming and laborious [20].

Conversely, one of the most promising top-down routes to graphene production for electroanalytical applications is direct exfoliation of graphite in an appropriate solvent. This approach utilizes low-cost and naturally abundant graphite as a source material, is simple to operate and easily scalable, the graphene sheets obtained typically comprise fewer than ten stacked layers and the resultant nanosheets tend to be defect-free (so that the intrinsic properties of graphene are largely retained) [20-22]. The disadvantage of the exfoliation method is that the nanosheets produced have broad thickness and lateral size distributions. Only one report of solvent-exfoliated graphene exists for the determination of caffeine but this utilizes a glassy carbon electrode support [23].

On the other hand, all the aforementioned publications dealing with the voltammetric determination of caffeine utilize a glassy carbon support for the graphene modification layer. Screen-printing is an electrode fabrication technology that presents many favorable properties for the

preparation of electrochemical sensors: screen-printed sensors are disposable, inexpensive, do not require cleaning/regeneration, are suitable for both surface and bulk modification, lend themselves to miniaturization and integration and can be rapidly mass-produced at low cost [24-27]. However, there is only a single report of the use of a screen-printed electrode modified with graphene for caffeine determination but, in this case, the graphene was produced by chemical reduction of graphene oxide [28].

The present work describes a new disposable three-electrode sensor for the determination of caffeine. The graphite working electrode of the sensor was drop-coated Nafion/graphene; the graphene was prepared by solvent exfoliation of graphite with N-methyl pyrrolidone (NMP). Caffeine was determined by anodic adsorptive stripping voltammetry. The proposed sensor combines many advantageous properties such as a high degree of integration, low cost, high sensitivity, disposability, fast and easy fabrication and modification and scope for operation in small sample volumes.

2. EXPERIMENTAL

2.1 Reagents

All the chemicals were of analytical reagent grade and purchased from Merck or Sigma-Aldrich unless stated otherwise. A 4.0 g L⁻¹ stock solution of caffeine was prepared from the solid compound in doubly distilled water and more dilute standards were prepared in doubly distilled water. Graphite flakes (+100 mesh) were supplied from Aldrich and were used without additional treatment before sonication. N-methyl pyrrolidone (NMP) was supplied from Aldrich. A 5 % (w/v) Nafion solution was purchased from Aldrich and more dilute solutions were prepared by dilution with absolute ethanol.

Samples of drinks, purchased from local stores, were purged with N₂ to remove CO₂ and properly diluted with the supporting electrolyte before analysis. For the instant coffee, 0.50 g of the sample was dissolved in 50 mL of hot water which was further diluted 1:1000 with the supporting electrolyte before analysis.

2.2 Instrumentation

For electrochemical experiments, an Autolab PGSTAT12/FRA2 electrochemical analyzer (Metrohm Autolab, Utrecht, The Netherlands) was used and in combination with the GPES software. A glassy carbon working electrode ($\varnothing = 2$ mm) was used for comparative measurements in combination with a Ag/AgCl (sat. KCl) reference electrode and a Pt wire counter electrode. The experiments were carried out in a 50 mL electrochemical glass cell while a magnetic bar rotated at approx. 1000 rpm provided stirring.

For scanning electron microscopy (SEM), a JSM-7401F instrument (JEOL, Tokyo, Japan) was used.

Raman scattering measurements were performed in the backscattering geometry using a RENISHAW inVia Raman microscope equipped with a CCD camera and a Leica microscope at room

temperature. A 2400 lines mm^{-1} grating was used for all measurements, providing a spectral resolution of $\pm 1 \text{ cm}^{-1}$. As an excitation source the Ar⁺ laser (514 nm with less than 0.5 mW laser power) was used. Measurements were taken with 120 s of exposure times at varying numbers of accumulations. The laser spot was focused on the sample surface using a long working distance 50× objective. Raman spectra were collected on numerous spots on the sample and recorded with a Peltier cooled CCD camera. The intensity ratio I_D/I_G was obtained by measuring the peak intensities following baseline correction.

For HPLC measurements, a LC-20AD HPLC instrument (Shimadzu) was used featuring a column oven (CTO-10AS VP), a degassing unit (DGU-20A5R) and a UV/Vis Detector (SPD-20A).

2.3 Sensor fabrication

Three-electrode sensors were fabricated by screen-printing on a flexible polyester sheet (0.175 mm thick, CUS7, Mac Dermid) using a semi-automatic screen printer (DEK 247), stainless steel screens (230 mesh, emulsion thickness 13 μm), and a 75 durometer polyurethane squeegee. The sensors were printed in using three steps: (i) silver printing (PF-410, Acheson) that serves as the conductive tracks of the three electrodes and as the reference electrode; (ii) graphite printing (PF-407A, Acheson) that serves as the working and auxiliary electrodes; (iii) dielectric printing (D2000222D2, Gwent) that serves as an insulating layer between the three electrodes. Each layer was allowed to dry for 30 min at 90 °C. The Ag reference electrode of the sensors was coated with AgCl by immersing the sensor into a 0.1 mol L^{-1} KCl solution, connecting the Ag and Pt electrodes to the anode and cathode, respectively, of a power supply and passing a current of 1 mA for 30 s.

2.4 Graphene preparation and sensor modification

0.25 g of graphene flakes was sonicated in 50 mL of NMP in a Bandelin Sonoplus Ultrasonic Homogenizer HD 3200 equipped with a flat head probe (VS70T), running at 10 % of maximum power (250 W) for 2 h. After that, the resulting suspension was centrifuged, washed with ultrapure water and ethanol several times, and finally dried in vacuum at 60°C for 5 h.

1.0 mg of graphene and 800 μL of ethanol were sonicated for 30 minutes. Then, 400 μL of a 0.5 % Nafion solution was added and sonication was continued for a further 30 min. A 5 μL drop of the modifying solution was applied to the working electrode of the sensor and left to dry for 30 min. When not in use, the sensor was stored in Britton Robinson buffer (pH 4.6) at 4 °C. For comparative measurements, a modifying solution not containing graphene was prepared by mixing 800 μL of ethanol and 400 μL of a 0.5 % Nafion solution.

2.5 Experimental Procedure

For the cyclic voltammetry experiments, 0.20 mol L^{-1} H_2SO_4 /0.010 mol L^{-1} HCl was used as the supporting electrolyte. Before each measurement, the solution in the cell was stirred for 20 s.

For adsorptive stripping analysis of caffeine, 20.0 mL of the 0.20 mol L⁻¹ H₂SO₄/0.01 mol L⁻¹ HCl supporting electrolyte was placed into the cell and adsorptive preconcentration was carried out at -0.2 V for 60 s under stirring. Then, the stirring was stopped and the solution was left to settle for 10 s. Voltammetric stripping was performed in the differential pulse (DP) mode in the potential range 0.70 to 1.70 V in order to record the background (base signal). DP conditions were the following: step potential, 8 mV; modulation amplitude, 80 mV; modulation time, 50 ms; interval time, 0.5 s. The procedure was repeated after addition of an aliquot of caffeine standard or sample. The peak current of the caffeine oxidation peak was monitored and related to the caffeine concentration in the cell.

For electrochemical impedance spectroscopy (EIS) experiments, the impedance spectra were recorded over the frequency range 10⁻¹ to 10⁵ Hz using a sinusoidal excitation signal with amplitude of 10 mV (rms) superimposed on a DC potential of +0.200 V (which is the equilibrium potential of the Fe(CN)₆⁻⁴/Fe(CN)₆⁻³ couple. EIS measurements were performed in a solution of 0.10 mol L⁻¹ KCl in the presence of 5.0 mmol L⁻¹ hexacyanoferrate (II) and 5.0 mmol L⁻¹ hexacyanoferrate (III) which was used as a redox probe.

3. RESULTS AND DISCUSSION

3.1 Characterization of the sensor

Raman spectroscopy is a powerful tool for studying graphene. Examination of a typical Raman spectrum of the exfoliated graphene reveals an increase of the intensity of the 1354 cm⁻¹ band (commonly referred to as the D-band) compared to the case of the Raman spectrum of pristine graphite flakes (Fig. 1). The D-band is associated with the number of sp³ defects introduced during the sonication process. The G band at 1582 cm⁻¹ is associated with sp² hybridized carbon atoms. In the case of exfoliated graphene, the ratio of the intensity of the D band over the intensity of the G band, I_D/I_G, is calculated as 0.21 (compared to 0.07 for pristine graphite) and provides a measure of the number of defects introduced through the sonication procedure with NMP. It is well established that sonication of graphite in a solvent will create defects into graphene sheets, however these are situated mostly on the edges, rather than on the graphene surface, leaving the electronic properties of the material mostly intact [29]. Broadening of the 2D band at ~2700 cm⁻¹ is indicative of few-layered graphene sheets, rather than single-layered graphene [29].

Inspection of the carbon working electrode with SEM clearly reveals the presence of the individual graphite particles (Fig. 2(A)). Modification with Nafion imparts a “cloudy” appearance to the electrode due to the presence of the polymeric film with the graphite particles still visible through the film (Fig. 2(B)). Modification of the electrode with graphene/Nafion causes a complete change in the SEM pattern. In this case, the graphene sheets predominate on the electrode surface completely covering it as demonstrated by the fact that the graphite particles are not visible any more (Fig. 2(C)).

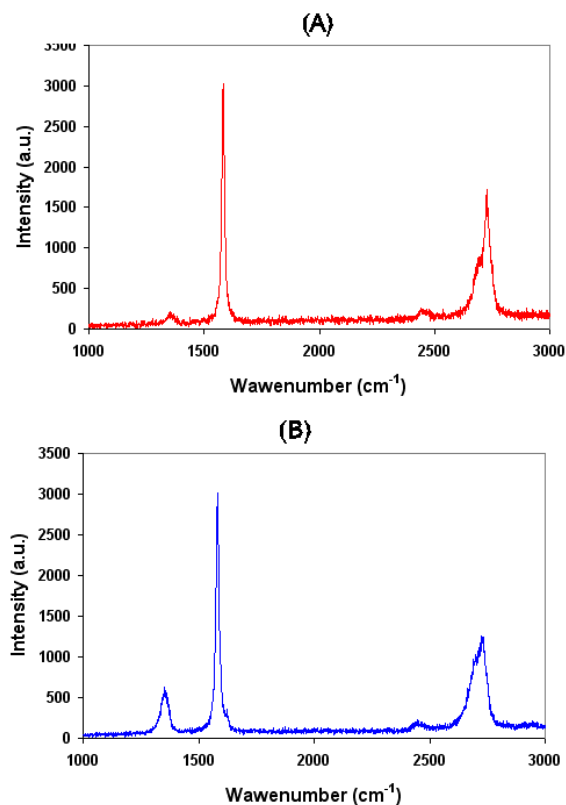


Figure 1. Raman spectra of: (A) pristine graphite, and; (B) exfoliated graphene after exfoliation by sonication in NMP for 1 h.

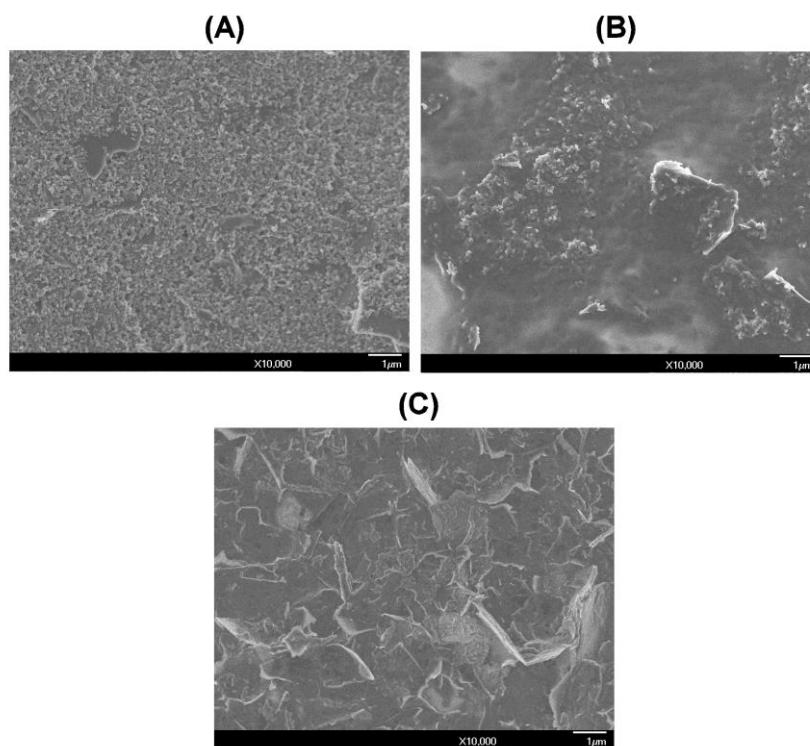


Figure 2. SEM images of the graphite screen-printed working electrode: (A) as prepared without modification; (B) after coating with Nafion, and (C) after coating with Nafion/graphene.

EIS plots of the bare, the Nafion-modified and the graphene/Nafion-modified screen-printed electrodes are illustrated in Fig. 3. Covering the bare graphite electrode with Nafion caused a substantial increase in the charge transfer resistance, as expected. However, the presence of graphene in Nafion reduced the charge transfer resistance of the electrode owing to the high conductivity of graphene [17].

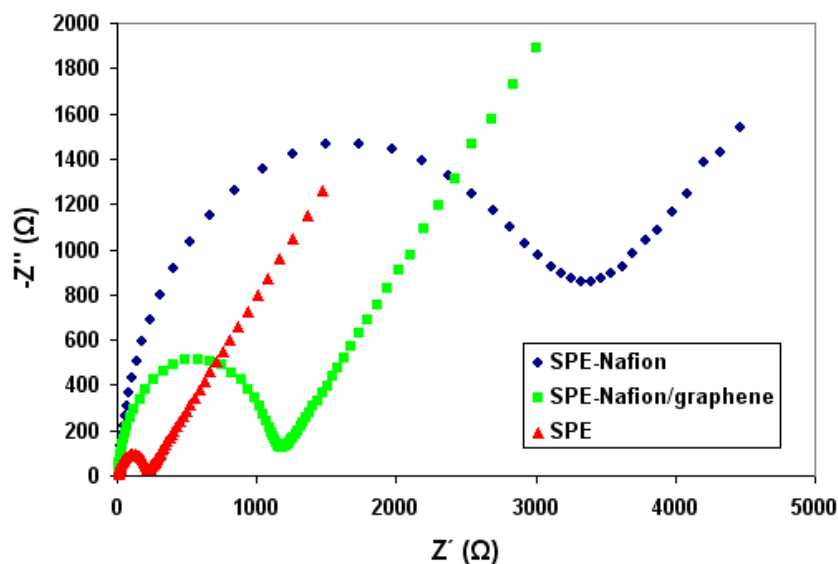


Figure 3. EIS of the bare, the Nafion-coated and the Nafion/graphene-coated graphite screen-printed working electrode.

Cyclic voltammetry experiments with the bare, the Nafion-modified and the graphene/Nafion-modified screen-printed electrodes for a solution containing $1.0 \mu\text{mol L}^{-1}$ caffeine were conducted in the potential range $+0.7 \text{ V}$ to $+1.7 \text{ V}$ (Fig. 4). When no accumulation was used (Fig. 4(A)), both the bare and the Nafion-modified electrodes produced very weak caffeine oxidation signals with the graphene/Nafion-modified screen-printed electrode yielding a substantially higher peak. In the case of adsorptive accumulation before the voltammetric step (Fig. 4(B)), the signal of the bare electrode remained unchanged. However, the caffeine oxidation peak increased at the Nafion-modified electrode; such enhancement of the caffeine oxidation signal at Nafion-modified electrodes has been observed before [23,30,31]. An even more substantial increase was observed at the graphene/Nafion-modified screen-printed electrode, as indeed noted in earlier work with a graphene/Nafion-modified glassy carbon electrode [13]. Therefore, the synergistic action of Nafion and graphene could be conveniently used for adsorptive accumulation of caffeine with the view to achieve higher sensitivity and lower limits of detection.

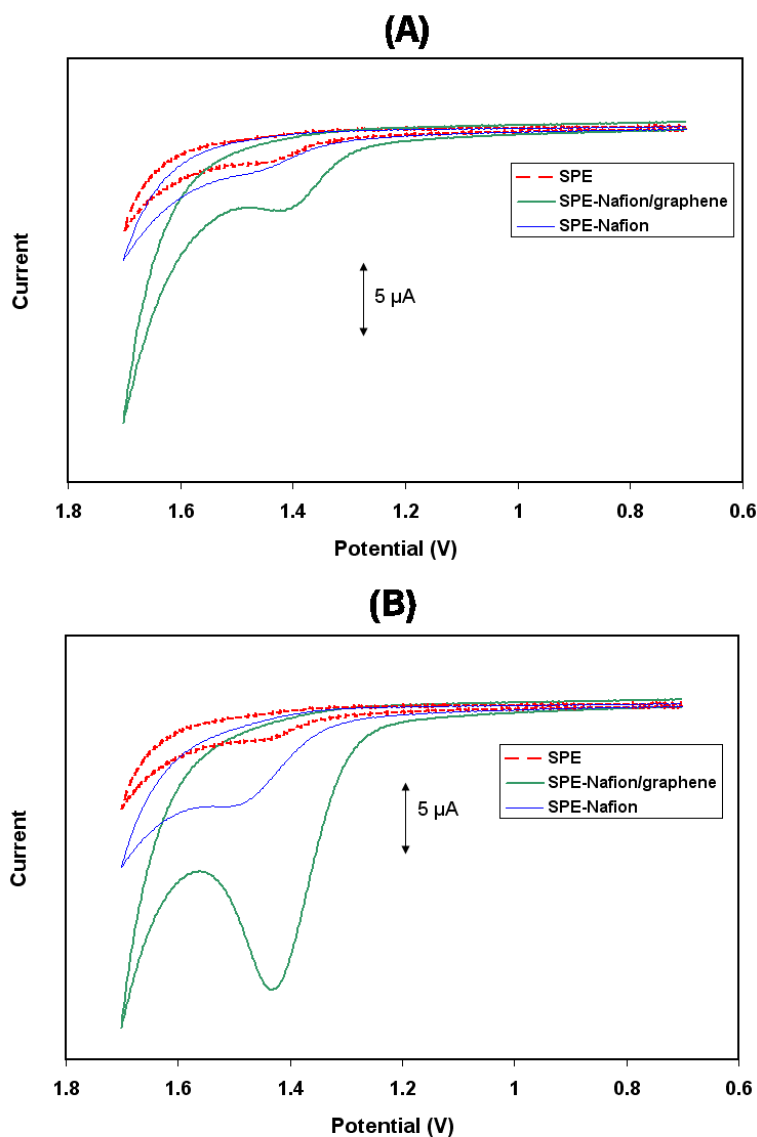


Figure 4. Cyclic voltammetry at bare, the Nafion-coated and the Nafion/graphene-coated screen-printed working electrode in a solution containing $1.0 \mu\text{mol L}^{-1}$ caffeine in $0.20 \text{ mol L}^{-1} \text{H}_2\text{SO}_4/0.010 \text{ mol L}^{-1} \text{HCl}$ in the range $+0.70 \text{ V}$ to $+1.70 \text{ V}$ (A) without preconcentration, and; (B) with preconcentration at 0.00 V for 120 s . CV conditions: step potential, 2.5 mV ; scan rate, 100 mV s^{-1} .

3.2 Evaluation of the sensor's analytical performance

Initially, the Nafion/graphene-coated graphite screen-printed working electrode was compared to a Nafion/graphene-coated glassy carbon electrode for the determination of caffeine by adsorptive stripping voltammetry (Fig. 5(A)). Both electrodes produced well-defined peaks with the graphite screen-printed electrode yielding higher sensitivity attributed to its higher surface area due to its greater roughness. Then, a comparison was made between different voltammetric waveforms (linear sweep (DC), differential pulse (DP) and square wave (SW)) for the stripping step (Fig. 5(B)). The

caffeine peak was sharper and the background was more favorable using the DP mode which was selected for subsequent experiments.

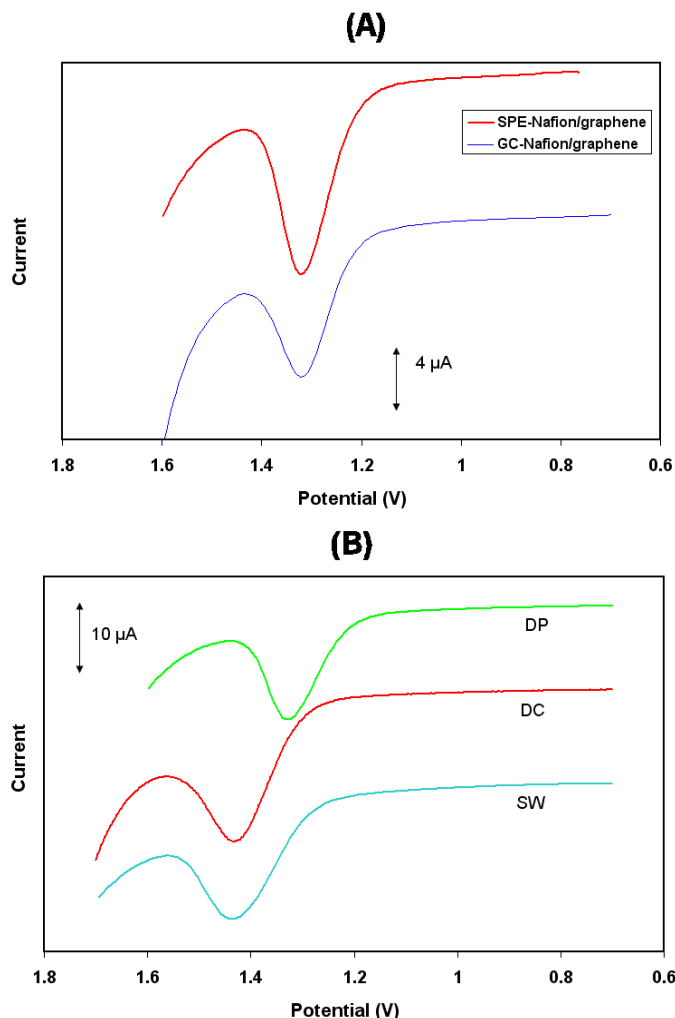


Figure 5. Comparison between: (A) the Nafion/graphene-coated graphite screen-printed electrode and a Nafion/graphene-coated glassy carbon electrode, and (B) linear sweep (DC), differential pulse (DP) and square wave (SW) waveforms for the determination of $1.0 \mu\text{mol L}^{-1}$ caffeine. Electrolyte, $0.20 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4/0.010 \text{ mol L}^{-1} \text{ HCl}$; deposition potential, 0.0 V ; deposition time, 120 s . DP conditions: step potential, 8 mV ; modulation amplitude, 80 mV ; modulation time, 50 ms ; interval time, 0.5 s . SW conditions: frequency, 25 Hz ; step potential, 8 mV ; amplitude, 25 mV . DC conditions: step potential, 2.5 mV ; scan rate, 100 mV s^{-1} .

Different acids (sulphuric, hyperchloric and phosphoric containing $0.01 \text{ mol L}^{-1} \text{ HCl}$) in the concentration range $0.10\text{--}1.0 \text{ mol L}^{-1}$ were assessed as supporting electrolytes with 0.20 mol L^{-1} of sulphuric acid producing the highest and more reproducible caffeine oxidation peak. Finally, a study of the deposition potential and deposition time was performed. Variation of the deposition potential in the range -0.40 V to $+0.40 \text{ V}$ revealed that the efficiency of the adsorptive accumulation was not substantially affected by the deposition potential (Fig. 6(A)). On the contrary, the deposition time had a dramatic effect on the caffeine oxidation current as the latter initially increased sharply with increasing deposition time and leveled-off at deposition times higher than 50 s (Fig. 6(B)). Based on these data, a deposition potential of -0.20 V and a deposition time of 60 s were selected.

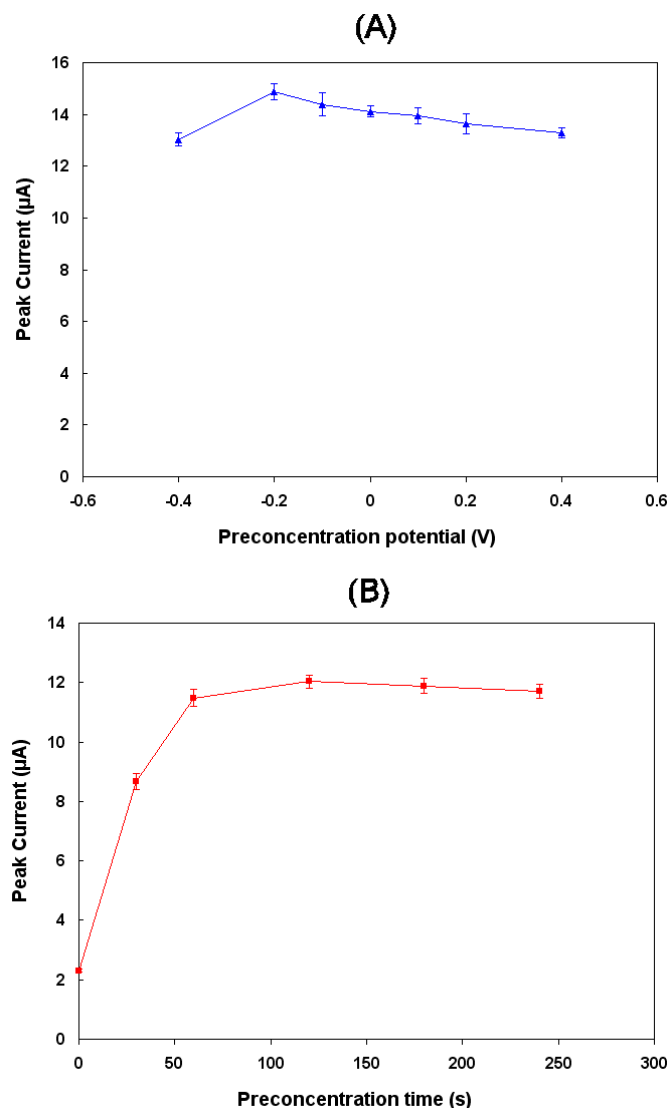


Figure 6. Study of: (A) the accumulation potential, and; (b) the accumulation time on the response of $1.0 \mu\text{g L}^{-1}$ caffeine. Electrolyte, $0.20 \text{ mol L}^{-1} \text{H}_2\text{SO}_4/0.010 \text{ mol L}^{-1} \text{HCl}$.

The analytical features of the proposed sensors were evaluated. Voltammograms for the determination of caffeine in two concentration ranges ($0.10\text{--}0.90 \mu\text{mol L}^{-1}$ and $1.0\text{--}10 \mu\text{mol L}^{-1}$) and the respective calibration plots are illustrated in Fig. 7. The linear range for caffeine determination with adsorptive accumulation for 60 s extended to $10 \mu\text{mol L}^{-1}$ but higher caffeine concentrations could be detected with lower accumulation times or with direct solution-phase voltammetry without accumulation. The limit of detection (LOD) (at $S/N=3$) for caffeine was $0.021 \mu\text{mol L}^{-1}$ and the limit of quantification (LOQ) was $0.066 \mu\text{mol L}^{-1}$. This LOD is one of the lowest reported in conjunction with graphene-based voltammetric sensors as (Table 1). The within-sensor reproducibility (expressed by the coefficient of variation for 8 consecutive measurements of $1.0 \mu\text{mol L}^{-1}$ caffeine at the same sensor) was 2.0 %. The between-sensor reproducibility (expressed by the coefficient of variation for

measurements of $1.0 \mu\text{mol L}^{-1}$ caffeine at five different sensors) was 11.6 %. The medium-term stability of the sensor was evaluated by analyses over a period of one week (the sensor was stored in Britton Robinson buffer (pH 4.6) at $4 \text{ }^\circ\text{C}$ between measurements). Although the response remained statistically stable for 1 week, the usual practice was to prepare a new electrode at the beginning of each working day.

Table 1. Applications of graphene-modified sensors for the voltammetric determination of caffeine.

Electrode	Graphene synthesis/Additional modifier	Detection technique	Sample	LOD ($\mu\text{mol L}^{-1}$)	Reference
GC	Chemical reduction of GO/CNTs	SWV	Chocolate, milk tea	0.02	[12]
GC	Chemical reduction of GO/Nafion	SWAdSV	Pharmaceuticals	0.031	[13]
GC	Electrochemical reduction of GO/melamine	DPV	Blood serum, urine	NR	[14]
GC	Electrochemical reduction of GO/poly(Alizarin Violet 3B)/CNTs	DPV	Blood serum	0.10	[15]
GC	Chemical reduction of GO/CTAB	DPV	Soft drinks	0.091	[16]
GC	Electrochemical reduction of GO/Nafion	DPV	Beverages	0.2	[17]
GC	Electrochemical reduction of GO/HDA	DPV	Blood serum, urine	0.43	[18]
GC	Electrochemical reduction of GO	DPV	Beverages, coffee, tea	NR	[19]
GC	Exfoliation in DMF/Nafion	DPV	Beverages, coffee	0.12	[23]
Screen-printed	Chemical reduction of GO/Nafion	Amperometry	Coffee	0.22	[28]
Screen-printed	Exfoliation in NMP/Nafion	DPAdSV	Beverages, coffee	0.021	this work

Abbreviations: GC, glassy carbon; GO, graphene oxide; CNTs, carbon nanotubes; SWV, square wave voltammetry; DPV, differential pulse voltammetry; DPAdSV, differential pulse adsorptive stripping voltammetry; SWAdSV, square wave adsorptive stripping voltammetry; CTAB, cetyltrimethylammonium bromide; DMF, dimethylformamide; NMP, N-methyl pyrrolidone; HAD, 1,6-hexadamine.

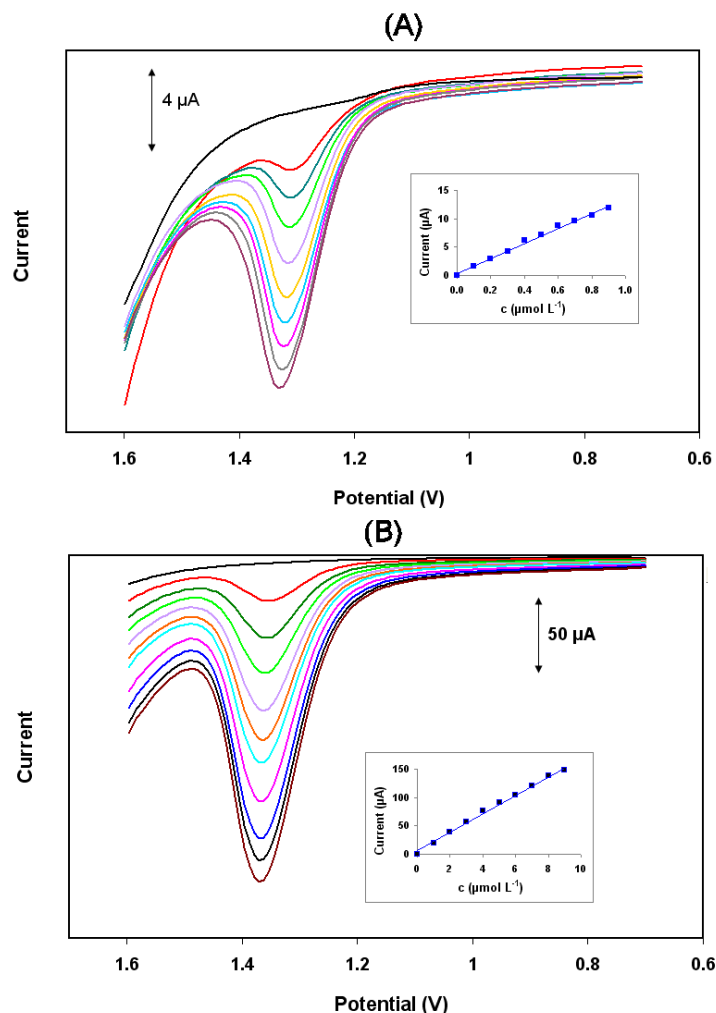


Figure 7. DP Voltammograms (and calibration plots as inserts) for caffeine in the range: (A) 0.10–0.90 $\mu\text{mol L}^{-1}$ (in steps of 0.10 $\mu\text{mol L}^{-1}$), and (B) 1.0–10 $\mu\text{mol L}^{-1}$ (in steps of 1.0 $\mu\text{mol L}^{-1}$) at the Nafion/graphene-coated graphite screen-printed using adsorptive stripping voltammetry. Electrolyte, 0.20 mol L^{-1} H_2SO_4 /0.010 mol L^{-1} HCl ; deposition potential, -0.20 V; deposition time, 60 s.

An interference study was conducted with respect to other compounds in typical beverage samples that could potentially interfere with the determination of caffeine. Citric acid, sucrose, fructose, maltose, K^+ , Na^+ , Ca^{+2} and SO_4^{-2} at 0.10 mmol L^{-1} did not interfere with the determination of 1.0 $\mu\text{mol L}^{-1}$ caffeine (the threshold of interference was set to $\pm 5\%$ change in the caffeine response).

The sensors were applied to the determination of caffeine in beverages, ice tea and instant coffee using the method of standard additions. The same samples were analyzed with HPLC and the results are summarized in Table 2. Statistical analysis of the data indicate that the results do not differ statistically between the two methods. Representative voltammograms and the standard additions plot for a coffee sample are illustrated in Fig. 8.

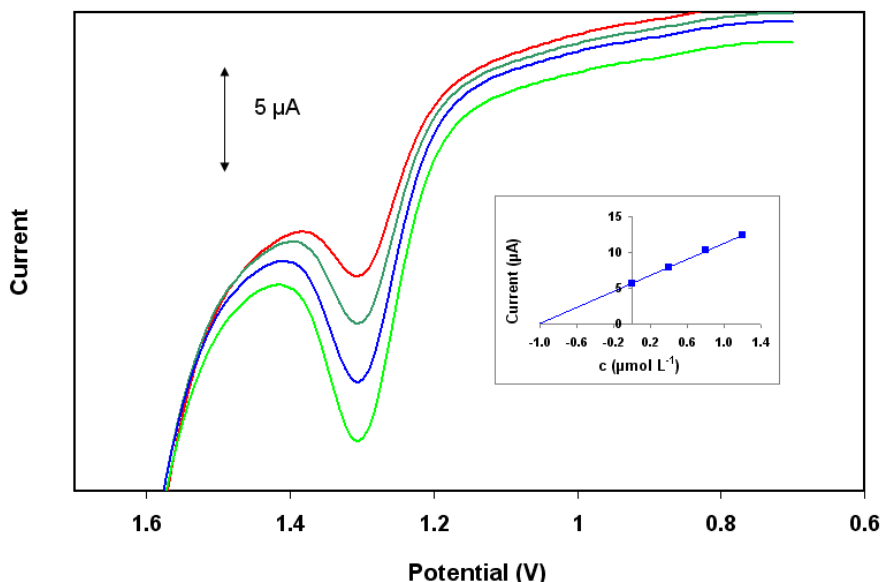


Figure 8. DP voltammograms for the determination of caffeine in a coffee sample using the method of multiple standard additions (standard additions plot as an insert). Electrolyte, 0.20 mol L⁻¹ H₂SO₄/0.010 mol L⁻¹ HCl; deposition potential, -0.20 V; deposition time, 60 s.

Table 2. Results for the determination of caffeine in various samples.

Sample	Caffeine found	Recovery (%)	Caffeine found (HPLC)
Energy drink 1 (mg L ⁻¹)	275 ± 31	105	266 ± 25
Energy drink 2 (mg L ⁻¹)	239 ± 22	101	247 ± 17
Cola drink (mg L ⁻¹)	136 ± 17	106	130 ± 10
Instant coffee (mg g ⁻¹)	39.6 ± 3.4	101	42.0 ± 3.0
Ice tea (mg L ⁻¹)	68 ± 8	106	60 ± 6

4. CONCLUSIONS

This work describes the fabrication of a “green” and low-cost graphene-modified screen-printed sensor. The screen-printed sensor comprises graphite working and auxiliary electrodes and a silver reference electrode. The working electrode is modified by drop-coating with Nafion/graphene. The graphene is synthesized using an efficient, simple, fast, inexpensive and “green” exfoliation approach in NMP. The synergistic effect of Nafion and graphene imparts adsorptive properties to the working electrode which can be exploited for analyte accumulation and leads to remarkable increase in sensitivity. An adsorptive stripping voltammetric procedure for caffeine is developed and application to caffeine determination in coffee and beverage samples show that the results did not differ statistically from HPLC which used as a reference method. In brief, the proposed sensor demonstrates fitness-for-purpose in fast quantitative screening of caffeine being highly integrated, inexpensive, sensitive, and easy to fabricate and to modify.

References

1. L.O. Porciúncula, C. Sallaberry, S. Mioranza, P. Henrique S. Botton and D.B. Rosemberg, *Neurochem. Int.*, 63 (2013) 594.
2. L.A.B. Persad, *Front. Neurosci.*, 5 (2011) 3.
3. P.N. Patil, *Int. J. Pharm. Sci. Rev. Res.*, 16 (2012) 76.
4. S.A. Bhawani, S.S. Fong and M.N.M. Ibrahim, *Int. J. Anal. Chem.*, 2015, Article ID 170239
5. L. Švorc, *Int. J. Electrochem. Sci.*, 8 (2013) 5755.
6. E.B. Bahadır and M.K. Sezginurk, *TrAC*, 76 (2016) 1.
7. A.T. Lawal, *Talanta*, 131(2015) 424.
8. D. Zheng, H. Hu, X. Liu and S. Hu, *Curr. Opin. Colloid. Interface Sci.*, 20 (2015) 383.
9. Y. Liu, X. Dong and P. Chen, *Chem. Soc. Rev.*, 41 (2012) 2283.
10. R.S. Edwards and K.S. Coleman, *Nanoscale*, 5 (2013) 38.
11. K.E. Whitener Jr. and P.E. Sheehan, *Diam. Relat. Mater.*, 46 (2014) 25.
12. L. Jiang, Y. Ding, F. Jiang, L. Li and F. Mo, *Anal. Chim. Acta*, 833 (2014) 22.
13. A. Yiğit, Y. Yardıma, M. Çelebi, A. Levent, Z. Şentürk, *Talanta*, 158 (2016) 21.
14. S. Kesavan, M.A. Raj and S.A. John, *Anal. Biochem.*, 496 (2016) 14e24.
15. Y. Wang, T. Wu and C.Y. Bi, *Microchim. Acta*, 183 (2016) 731.
16. J.Y. Sun, K.J. Huang, S.Y. Wei and Z.W. Wu, *Can. J. Chem.*, 89 (2011) 697.
17. F. Zhao, F. Wang, W. Zhao, J. Zhou, Y. Liu, L. Zou and B. Ye, *Microchim. Acta*, 174 (2011) 174.
18. M.A. Raj and S.A. John, *Anal. Chim. Acta*, 771 (2013) 14.
19. W. Yu, H. Khoo, M. Pumera and A. Bonanni, *Anal. Chim. Acta*, 804 (2013) 92.
20. Y. Wei and Z. Sun, *Curr. Opin. Colloid. Interface Sci.*, 20 (2015) 311.
21. L. Niu, J.N. Coleman, H. Zhang, H. Shin, M. Chhowalla and Z. Zheng, *Small*, 12 (2016) 272.
22. J.N. Coleman, *Accounts Chem. Res.*, 46 (2013) 14.
23. J.Y. Sun, K.J. Huang, S.Y. Wei, Z.W. Wu and F.P. Ren, *Colloids and Surfaces B: Biointerfaces*, 84 (2011) 421.
24. A. Hayat and J.L. Marty, *Sensors*, 14 (2014) 10432.
25. M. Li, Y.T. Li, D.W. Li and Y.T. Long, *Anal. Chim. Acta*, 734 (2012) 31.
26. F. Arduini, L. Micheli, D. Moscone, G. Palleschi, S. Piermarini, F. Ricci and G. Volpe, 79 (2016) 114.
27. C.E. Banks, C.W. Foster and R.O. Kadara, *Screen-Printing Electrochemical Architectures*, Springer International Publishing, (2016)
28. I. Vasilescu, S.A.V. Eremia, R. Penu, C. Albu, A. Radoi, S.C. Litescu and G.L. Radu, *RSC Advances*, 5 (2015) 261.
29. Y. Hernandez, V. Nicolosi, M. Lotya, F.M. Blighe, Z.Y. Sun, S. De, T. McGovern, B. Holland, M. Byrne, Y.K. Gunko, J.J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A.C. Ferrari and J.N. Coleman, *Nat. Nanotechnol.*, 3 (2008) 563.
30. C.A. Martínez-Huitle, N. Sueily Fernandes, S. Ferro, A. De Battisti and M.A. Quiroz, *Diam. Rel. Mater.*, 19 (2010) 1188.
31. B. Brunetti, E. Desimoni and P. Casati, *Electroanalysis*, 19 (2007) 385.