

Amperometric Detection of Gallic Acid Based on Electrochemically Activated Screen Printed Carbon Electrode

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A simple electrochemical sensor based on activated screen printed carbon electrode (ASPCE) was successfully fabricated for the selective and sensitive amperometric determination of gallic acid (GA). The activated screen printed carbon electrode (ASPCE) was fabricated by simple electrochemical technique and it was characterized by using scanning electron microscopy (SEM), Raman spectroscopy and electron impedance spectroscopy (EIS). The electrochemical properties of the electrodes were investigated by the cyclic voltammetry and amperometric method. Interestingly, ASPCE exhibited an excellent electrocatalytic activity in terms of decrease the potential and increase the anodic peak current for the detection of GA when compared to bare SPCE. The ASPCE was successfully determined the GA and it showed good wide linear response range from 0.01 to 1799.6 μM and the lowest detection limit (LOD) of 0.031 μM . Moreover, the fabricated sensor electrode was manifested a good selectivity, stability, repeatability and reproducibility. The sensor was applied to the determination of GA in real samples, where it shows good recovery and accuracy. To the best of our knowledge, this electrode is cost effective and excellent performance towards the detection of GA when compared with previously reported other chemically modified electrodes.

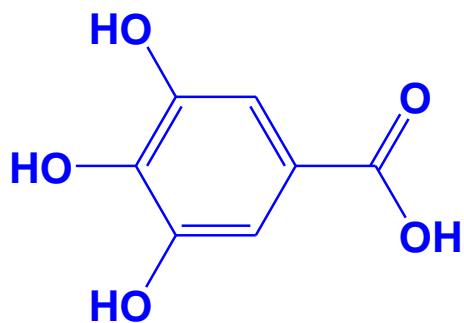
Keywords: Gallic acid, Amperometric technique, Cyclic voltammetry, Activated screen printed carbon electrode.

1. INTRODUCTION

Gallic acid (GA) is one type of phenolic compounds that have been widely present in the grapes, blueberries, walnuts, apples, green tea, watercress, black tea, oak bark and herbs [1]. GA has a number of properties such as anti-mutagenic, anticancer, anti-inflammation, antioxidant and these are used to preventing (against diseases) human health in day to life [2]. And also, GA possessed a

numerous advantages have been reported previously for the GA, but the dosage of age is very important for human health. The overdoses of GA present in our body which leads to causes some severe diseases. Normally, the GA is highly interfering with blood pressure drugs, very risk for a heart problem and it was previously reported [3]. For aforementioned reason, the accurate level detection of GA is very important concern for human health. Up to now, a number of techniques have been developed for the determination of GA including flow injection analysis [4], photo electrochemical platform [5], resonance light scattering [6], thin-layer chromatography [7] and electrochemical techniques [8-10]. Among all, electrochemical techniques have a number of advantages such as high sensitivity, selectivity, low cost, user friendly and quick response when compare with other traditional methods [11-13].

There are number of electrodes have been developed and applied for the detection of GA, particularly carbon based materials, such as carbon paste electrodes [14], graphite electrodes [15], carbon fiber microelectrodes [16], glassy carbon electrodes (GCE) [17], carbon ionic liquid electrodes [18], and screen-printed electrodes [19]. Among them, Screen-printing technology represents a well-developed technique for the fabrication of electrode with mass production, highly reproducible manner, flexibility, and easily disposable [20]. Especially, Screen-printed carbon electrode (SPCE) has transfigured not only by low cost but also good electrochemical sensing properties [21]. For improved detection selectivity and sensitivity is achieved by increasing the surface with groups of oxygen functionalities and generation of edge plane like site grafting the surface using electrochemical techniques [22-24]. The main objective of this work is to develop a cost effective, selective and sensitive method for the amperometric determination of GA by using anodized SPCE for the first time. The anodized SPCE was characterized by different physicochemical characterizations. It showed the high electrocatalytic activity towards GA.



Scheme 1. Structure of gallic acid (GA)

2. MATERIALS AND METHODS

2.1. Materials

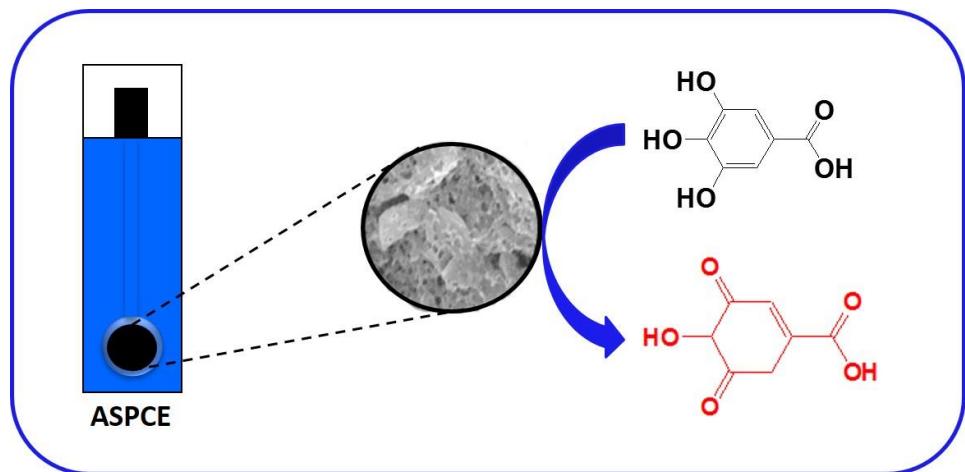
Screen printed carbon electrode (working area = 5 mm) were purchased from Zensor R&D Co., Ltd, Taiwan. Gallic acid (GA), acetaminophen (AC), hydroquinone(HQ), dopamine (DA), ascorbic acid (AA), uric acid (UA), ferulic acid (Sigma- FA), catechol (CT) morin (MR), salicylic acid (SA),

sodium hydrogen phosphate (NaHPO_4), sodium hydroxide (NaOH), sodium dihydrogen phosphate (NaH_2PO_4) and all other chemicals were obtained from Aldrich and used without any additional purification. Double distilled (DD) water were obtained from a Millipore purification system.

The structure and surface morphological study was investigated by using scanning electron microscopy (SEM Hitachi S-3000 H). Raman spectra were recorded using a Raman spectrometer (Dong Woo 500i, Korea) equipped with a charge-coupled detector. Cyclic voltammetry (CV) and amperometry experiments were executed by using CHI 750A work station (Inc. Made in U.S.A). Electrochemical impedance spectroscopy (EIS) by ZAHNER Scientific Instruments (THALES software package). Electrochemical studies were carried out in a conventional three electrode system using ASPCE as a working electrode (area 5 mm), a platinum wire as a counter electrode and saturated Ag/AgCl (saturated KCl) as a reference electrode. All the electrochemical measurements were carried out at room temperature.

2.2. Methods

The ASPCE was fabricated by our previously reported method with slight modification [25]. In briefly, 0.1 M of NaOH was prepared by using DD water. Thereafter, the SPCE was immersed into an electrochemical cell containing 0.1 M NaOH , followed by the fixed (applied) potential from 0 to 2.0 V up to 10 cycles for activation of SPCE. Finally, the obtained activated SPCE was used for further electrochemical measurements.



Scheme 2. Oxidation mechanism of gallic acid (GA)

3. RESULTS AND DISCUSSION

3.1 Characterization of ASPCE

The surface morphology of electrode was investigated by SEM. Fig.1 shows the SEM images of (A) SPCE and (B) ASPCE. From the Fig. 1A, it was clearly observed that the activation (before) of SPCE shows a rough and aggregated flake like morphologies [19]. After the activation of SPCE the

surface morphologies was totally changed into porous like structure, which indicates that the bare SPCE was successfully activated (ASPCE). A Raman spectrum is one of the important non-destructive tools for carbon material. Fig. 1C shows the Raman spectrum of (a) SPCE and (b) ASPCE. The Raman spectra exposed two peaks at around 1255 cm^{-1} and 1500 cm^{-1} which indicates D (disordered) and G (graphitic) band respectively. Furthermore, intensities ratio value (I_D/I_G) for the SPCE was 1.169 and ASPCE was 0.89 which is directly proportional to the disorder in its hexagonal lattice [19].

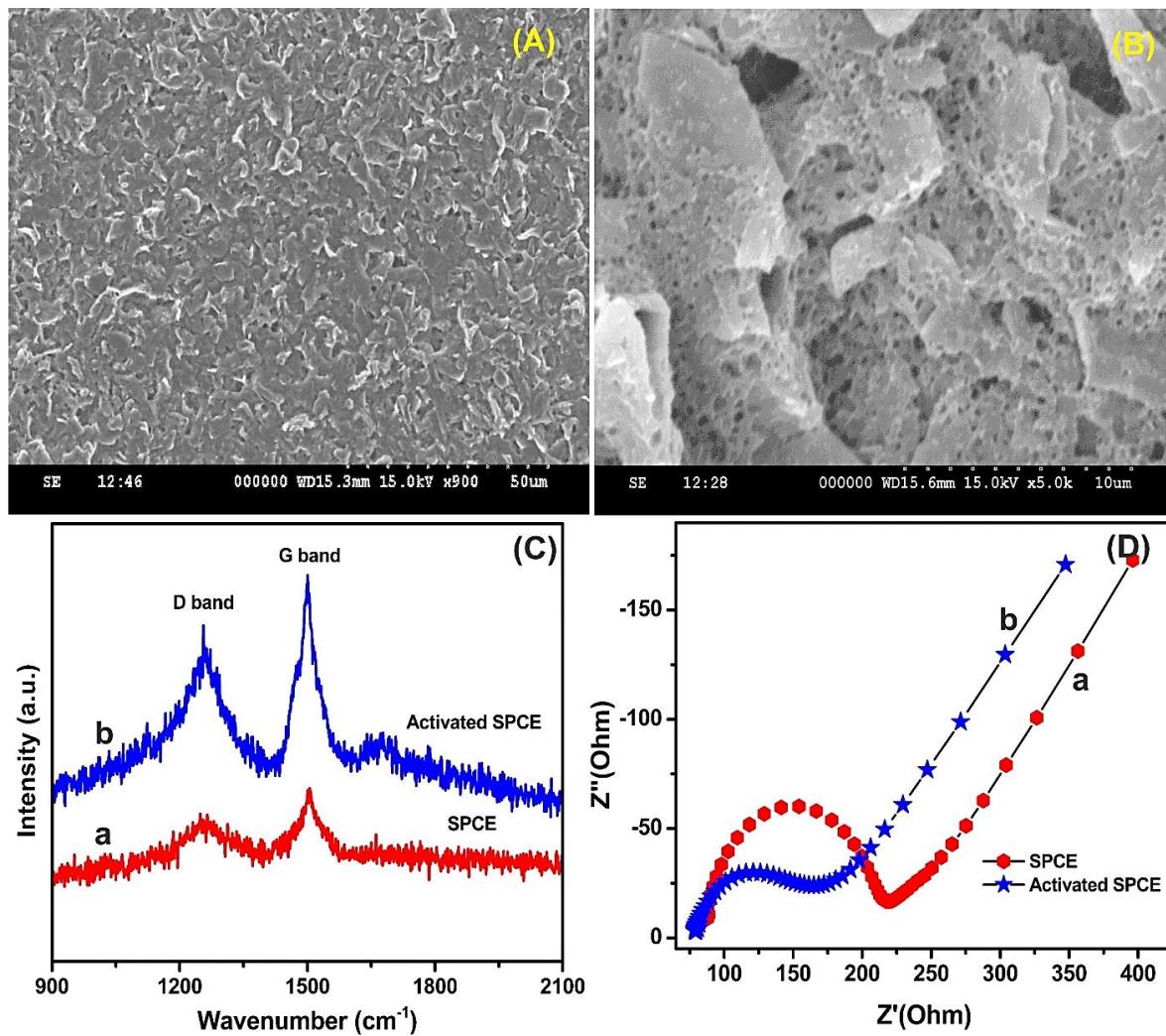


Figure 1. SEM images of (A) SPCE (B) ASPCE (C) Raman spectra of (a) SPCE and (b) ASPCE (D) EIS of (a) SPCE and (b) ASPCE.

Electrochemical impedance spectroscopy (EIS) is an extremely efficient analytical technique for providing the details about electrical conductivity and electron transfer properties between electrode surface and electrolytes. Fig. 1D displays the nyquist plots of (a) SPCE (b) ASPCE were recorded in $[\text{Fe}(\text{CN})_6]^{3/4}$ system containing 0.1 M KCl solution. The EIS results are analyzed by using randle equivalent electrical circuit model. From the Fig.1D (a) is clearly observed that the bare SPCE shows a large semicircle which is due to the slow electron transfer (High resistance and the R_{ct} value is = 131.2Ω). After that, the activation in 0.1 M NaOH obtained ASPCE (low resistance and the R_{ct} value is = 81.4Ω).

Ω) shows a small semicircle when compared to bare SPCE which is due to the fast electron transfer between electrode surface and electrolytes as it shown in Fig.1D (b). The all obtained results, which is good agreement with the SEM images.

3.2 Electrochemical behavior of GA

The electrocatalytic behavior of different modified electrodes was investigated by using CV. Fig. 2A shows the electrochemical performance of GA on (a) SPCE (c) ASPCE in the absence and (b) SPCE (d) ASPCE in the presence of 200 μ M GA containing 0.05M PB solution (pH 7) at a scan rate 50 mV/s. CV response of the test solution in absence of GA at bare SPCE (curve a)/ASPCE (curve b) and it can be seen Fig. 2A. It can be seen that, there is no oxidation peak was observed in the absence of GA (Fig.2A (a, c)), indicating that the bare SPCE/ASPCE is electrochemically inactive in the potential window range from -0.2 to 1 V. At the same time, in the presence of 200 μ M GA at SPCE shows a broad anodic oxidation peak current at the longer potential of 0.6 V, and the oxidation peak current is very lower when compared to ASPCE. On the other hand, in the presence of 200 μ M GA at ASPCE shows a sharp and well-defined anodic peak current was observed at the potential of 0.47 V, suggesting that the activated SPCE provided large surface area (oxygen functionalities and grafted through NaOH) and enhancing the peak current for the detection of GA. For comparison, the obtained anodic peak current at ASPCE is 4.5 folds higher when compared to bare SPCE and very lower positive potential was also observed when compared with bare SPCE. From the CV results, first oxidation peak was ascribing to the formation of the semiquinone, followed by its second oxidation to the quinone form, but the second oxidation is not so distinct. Henceforth, ASPCE is high catalytic activity towards GA than the other modified electrodes.

3.2.1 Effect of pH

The electrochemical system should be affected by change in pH value. In order to investigate the influence of pH (1.0-9.0) was studied in the presence of 200 μ M of GA at ASPCE and the results are shown in Fig.2B. The anodic peak current of GA was gradually decreased while increasing pH (pH 1.0 to 9.0) and the anodic peak potential of GA was also shifted towards more negative values. The peak current of pH 1.0, 3.0 are nearly similar and pH 3.0 is peak potential is lower when compared to pH 1.0. Hence, the pH 3.0 was chosen for the electroanalytical determination of GA.

3.2.2 Effect of Scan Rate

Fig. 2C revealed the effect of scan rate on the electrochemical performance of 200 μ M GA at the ASPCE in 0.05M PB (pH 3.0) with different scan rate ranging from 10 to 100 mV/s. From the figure, the oxidation peak currents linearly increased with increasing the scan rates and the peak potential was slightly shifted to negative side. The linear relationship plot was fitted against anodic

peak current vs. scan rate (Fig. 2D) with correlation coefficient of $R^2=0.9903$. These obtained results suggested that the electrochemical oxidation of GA at ASPCE is an adsorption controlled process [1].

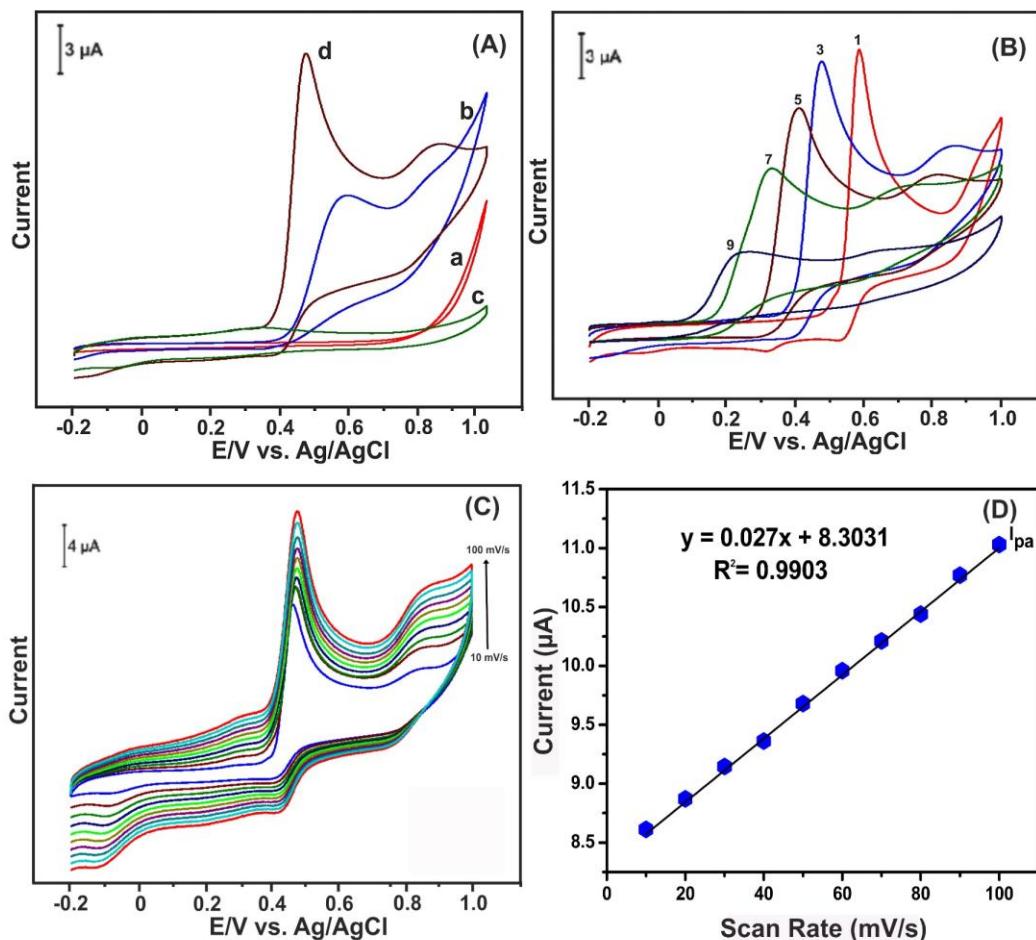


Figure 2. (A) CV response of (a) SPCE (C) ASPCE in the absence (b) SPCE (d) ASPCE in the presence of 200 μM of GA containing 0.05M PBS (pH 3.0) at a scan rate of 50 mV/s. (B) CV response of GA on ASPCE in various pH ranges from 1.0 to 9.0 containing 0.05M PB solution. (C) CVs of GA oxidation on ASPCE for various scan rates from 10 to 100 mV/s. (D) The relationship between peak current vs. scan rate.

3.2.3 Amperometric detection of GA

Fig. 3A depicts the amperometric response of ASPCE for the successive additions of GA for various concentrations ranging from 0.001 μM to 14 mM for sequential injected at regular intervals (50 s) into continuously stirred 0.05 M PB (pH 3.0) solution. The applied electrode potential was held at 0.470 V, with rotation speed was fixed at 1200 rpm. The oxidation peak current of GA was increased with increasing the concentrations. The oxidation peak current of the GA was plotted against the concentration of GA and shown in Fig. 3B, it exhibits the linearity from 0.01 μM to 1799.6 μM with the linear correlation coefficient of $R^2 = 0.9984$. From the calibration plot, the lower detection limit (LOD) of GA was calculated to be 0.031 μM . The obtained electro-analytical parameters at ASPCE

such as wide linear ranges and LOD are summarized in Table 1. The presented electro-analytical parameters at ASPCE towards GA which are very comparable with previously reported GA sensors.

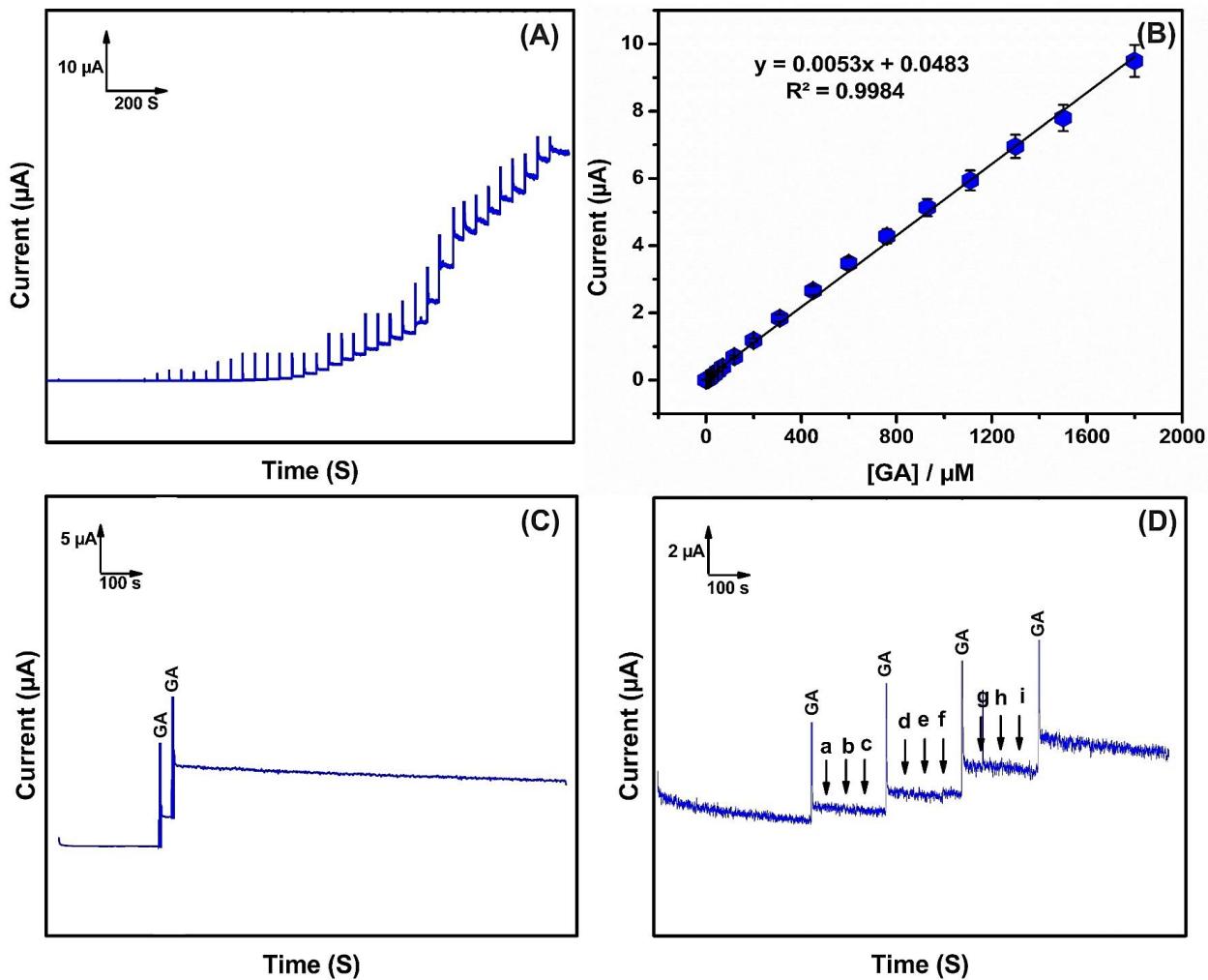


Figure 3. (A) The amperometric response of ASPCE with different concentration of GA in 0.05 M PBS (pH 3) from 0.001 μM to 14 mM., (B), The plots of peak current of GA vs. its concentration (C) The amperometric response of GA in ASPCE attaining the steady state current, (D) The amperometric response of GA with the 10-fold excess interfering compounds such as CT (a), HQ (b), DA(c), AA (d), UA (e), FA (f), AC (g), MR (h) and GA (i).

3.2.3 Stability

The stability of the ASPCE were studied by using amperometric technique. Fig.3D shows the amperometric responses of GA oxidation at ASPCE with the addition of 0.01 mM GA in 0.05 M PB solution for the steady state current response up to 1800 s with a working potential of 0.470 V. The ASPCE shows 93.3% retention response from the initial current response. The results endorsed that the ASPCE have good stability and it can be used for the practical applications.

Table 1. comparison on the analytical performance of ASPCE with previously reported detection of GA.

Electrode	Method	Linear range (μM)	LOD (μM)	Ref
GCE/LDHf	DPV	4-600	1.6	26
CPE/SiO ₂	DPV	0.8-100	0.25	27
CPE/MWCNT-Fe	DPV	0.5-15	0.3	28
CPE/MWCNTb pH 2	DPV	1-33.75	0.27	29
AgNP/Delph/GCE	Amperometry	0.60-625.80	0.28	30
GCE	DPV	-	-	31
GCE/PEI-rGO	LSV	0.058-580	0.3	32
GE/TH/NiHCF	Chronoamperometry	4.99-1200	1.66	33
GCE/MWCNT	Chronoamperometry	100-1300	0.144	34
TiO ₂ /CPE	DPV	2.5-150	0.94	35
MCPE/CNT	Amperometry	0.5-150	0.3	36
GCE/PEP	DPV	1-20	0.06	37
GCE-Tyr-nAu	DPV	25-900	0.7	38
ASPCE	Amperometry	0.01 - 1799.6	0.031	This work

3.2.4 Interference study and real sample analysis

Selectivity playing an important role in electrochemical sensors, hence the amperometric interference studies was evaluated in the presence of potentially interfering compounds. The amperometric technique was estimated to analysis the selectivity of GA which taken at 0.470 V. Fig. 3D shows the amperometric responses of GA with 10-fold excess concentration of interfering ions such as CT (a), HQ (b), DA(c), AA (d), UA (e), FA (f), AC (g), MR (h) and GA (i). This resulted indicated their no such distinct response for the interference compounds. This study confirmed that ASPCE was more suitable for the determination of GA in practical applications.

Table 2. Detection of gallic acid in green tea and apple juice

Beverage type	Added (μM)	Found (μM)	Recovery (%)	RSD (%)
Green tea	-	23.2	-	-
	5	28.9	102.4	1.6
Apple juice	-	48.2	-	-
	5	55.6	104.5	2.1

In order to evaluate the real time application of the proposed sensor was measurement of GA in green tea and apple juice amperometry. The experimental parameters are similar to Fig. 3A. The standard addition method was used for calculation of recovery of GA in green tea and apple juice. The content of GA in green tea and apple juice were found as 23.2 and 48.2 μM . Then, a known

concentration GA containing real samples were injected into the supporting electrolyte solution and the detection results are listed in Table 2. The detection recoveries in the range of 102.4 % and 104.5 % with acceptable relative standard deviations (RSD). Hence, the proposed sensor exhibited significant accuracy and recovery values in real samples.

4. CONCLUSION

In conclusion, we successfully fabricated Pre-anodized screen printed carbon electrode (ASPCE) by simple electrochemical technique. ASPCE was characterized by SEM, Raman Spectra, EIS and electrochemical method. It is a simple and robust electrochemical sensing platform for cost effective, fast response, good sensitive, high selective including low detection limit, wide linear range, stability. Furthermore, the proposed sensor was successfully used for the determination of GA in real samples. The ASPCE is simple to fabricate and low cost electrodes for detection of GA.

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