Determination of gallic acid using poly(glutamic acid): graphene modified electrode

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MS received 25 September 2018; revised 9 December 2018; accepted 18 December 2018; published online 19 January 2019

Abstract. Gallic acid (GA) is one of the main phenolic components occurring naturally in plants and has been a subject of increasing interest owing to its antioxidant, anti-mutagenic and anti-carcinogenic properties. The present work describes a rapid and cost-effective analytical procedure for the determination of gallic acid. Poly-Glu/rGO electrode was fabricated by the electro-polymerisation of glutamic acid on reduced graphene oxide (rGO) modified paraffin impregnated graphite electrode (PIGE). The modified electrode was characterized by SEM, AFM and ATR-IR. The electrochemical behavior of gallic acid at the modified sensor was studied by voltammetric and amperometric techniques under optimized conditions in pH 5 acetate buffer. The electrode showed good linear response towards the determination of gallic acid over the range of 0.03–480 μM with 0.01 μM as the detection limit for voltammetric technique and the amperometric technique showed a linear range of 1–17 μM with 0.33 μM as the detection limit. The electrode also showed good stability and reproducibility with a sensitivity of 0.97 $\mu\text{M}/\mu\text{A}$. The proposed method can be applied to detect GA in real samples with satisfactory results.

Keywords. Poly glutamic acid; modified electrode; gallic acid and electrochemical sensor.

Abbreviations

rGO	Graphene
Poly-Glu	Poly glutamic acid
GA	Gallic acid

1. Introduction

Gallic acid (GA) also known as 3,4,5-trihydroxy benzoic acid belongs to a large family of secondary polyphenolic metabolites widely present in the plant kingdom. It occurs in natural products such as gall-nut, blueberries, apples, flaxseeds, tea leaves, oak bark, walnuts and watercress. It possesses antioxidant, anti-inflammatory, anti-microbial, radical scavenging properties and also DNA polymerase and ribonucleotide reductase activity.^{1,2} Its supplements are available as capsules, ointments and liquid extracts and have been used traditionally to treat a variety of ailments. Gallic acid is widely used in processed food, cosmetics and food packing materials as it prevents rancidity due to lipid peroxidation and spoilage.³ It is usually

obtained through the alkaline or acid hydrolysis of tannins or hydrolysis of spent broths derived from *Penicillium glaucum* or *Aspergillus niger*. It has also been reported to possess cytotoxic effect against isolated hepatocytes.^{4,5} Given its biological importance gallic acid detection becomes pertinent.^{6,7}

Graphene is the fundamental building element of many carbon allotropes including graphite, charcoal, carbon nanotubes, buckminster fullerene and other buckyballs. Graphene comprises a single layer of six-atom rings in a honeycomb network and can be conceptually considered as a true planar aromatic macromolecule.⁸ Graphene oxide exhibits interesting optical properties,⁹ chemical versatility and the tunable functional groups on the Graphene oxide (GO) surface makes GO an ideal platform to immobilize a variety of biomolecules including nucleic acids, peptides, proteins and has demonstrated its potential in electrochemical biosensors applications.^{10–12} Tailoring the electronic solid state properties of these carbon allotropes through chemical functionalization would improve its catalytic performance.¹³

Recent research has focused attention towards polymer-modified electrodes as they possess propitious

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characteristics such as more active sites, excellent perm-selectivity, good stability and strong adherence towards electrode surface.^{14,15} Biopolymers prove to be more promising sensing platform in comparison to synthetic polymers as they are bio-compatible and biodegradable.^{16–18} Poly-Glutamic acid (Poly-Glu) is one such biopolymer with various biological functions and promising properties for basic and applied research.^{19–26} Poly-Glu is known to promote electron transfer and also provide conducting bridges.^{27–29} It consists of various units of Glutamic acid connected through γ -peptide linkages and the α -carboxyl groups are free to bind with a wide range of compounds.^{29–31}

Herein, the analytical utility of Poly-Glu/rGO modified electrode as a sensing platform has been reported for the selective determination of Gallic acid through a constructive combination of the large surface area of Graphene and the strong sensing ability of Poly-Glutamic acid.

2. Experimental

2.1 Chemicals and reagents

Glutamic acid and Graphite powder were purchased from Sigma-Aldrich, USA. Graphite rods of 0.3 cm diameter and length of 4.0 cm were purchased from Aldrich, USA. All other reagents were of analytical grade and were used as received without any further purification. Doubly distilled water was used throughout the experiments.

2.2 Instrumentation

All electrochemical experiments were performed on a CHI 660B electrochemical workstation (CH Instruments, USA) comprising a conventional three-electrode system consisting of a platinum wire as an auxiliary electrode, saturated calomel as reference electrode and a bare Paraffin impregnated graphite electrode (PIGE) or PIGE/rGO/Poly-Glu modified electrode as the working electrode. All the experiments were carried out at room temperature. The SEM experiments were made on a VEGA3 TESCAN instrument, ATR-IR measurements using Thermo Scientific Nicolet iS5 with iD3 ATR-IR spectrometer and AFM images were recorded on MFP-3D Infinity ASYLUM Research instrument.

2.3 Fabrication of Poly-Glu/rGO electrode

2.3a Electrochemical reduction of GO: Initially, graphite rods were impregnated with paraffin according to the previously reported procedure to form PIGE.³² Then, an ethanolic solution of graphene oxide synthesized by modified Hummer's method³³ was drop casted onto the surface of PIGE and allowed to dry for few hours at room temperature. The electrode was further subjected to a reduction potential

Figure 1. Electro-polymerization of Glutamic Acid on rGO electrode surface obtained by scanning potentials between -0.8 and 2 V for 20 cycles (scan rate of 50 mV/s in PBS at pH-7 containing 0.02 M Glutamic acid).

of -1.2 V over a period of 900 s in 0.1 M Phosphate buffer solution (PBS) of pH-7.0 using chronoamperometry technique to obtain rGO/PIGE modified electrode.³⁴

2.3b Electro-polymerization of Glutamic acid on rGO modified electrode surface: The rGO modified electrode was placed in PBS-7.0 containing 0.02 M Glutamic Acid and electropolymerization of glutamic acid was achieved by cycling potential from -0.8 to 2.0 V for 20 cycles³⁵ as shown in Figure 1. The electrode was then removed and the surface was rinsed with double distilled water to remove the excess monomer and the electrode obtained was labeled as Poly-Glu/rGO modified electrode.

The surface coverage concentration of the poly-Glu/rGO modified electrode has been calculated by the following equation.³⁶

$$\tau = \frac{Q}{nFA} \quad (1)$$

where τ indicates the surface coverage (mol cm^{-2}), Q is the quantity of charge (C), n is the number of electrons transfer, A is the electrode surface area (cm^2) and F is Faraday constant (96485.3329 C mol^{-1}). From equation (1), the surface coverage concentration of the poly-Glu/ rGO modified electrode was calculated to be $4.598 (\pm 0.018) \times 10^{-9}$ mol cm^{-2} .

3. Results and Discussion

3.1 Electro-Polymerization of Glutamic acid on rGO surface

The Poly-Glu/rGO was prepared by placing the rGO/PIGE in PBS-7.0 containing 0.02 M Glutamic Acid and electro-polymerized at a potential range from -0.8 to 2.0 V for about 20 cycles. On the first scan, we

Figure 2. (a) SEM of the rGO modified surface and (b) Poly-Glu/rGO modified electrode surface.

observed an oxidation peak at about 1.65 V similar to the reports by some researchers^{35,37} which was attributed to the mass electro-polymerization of Glutamic acid on the electrode surface which almost vanished completely in the subsequent cycles. But, the anodic current increases gradually on cycling due to the formation of an electroactive layer of polymer film on the electrode surface and it remains almost constant after the 16th cycle suggesting the level of saturation of polymer growth. Glutamic acid condenses due to the interaction between the amino group ($-\text{NH}_2$) and a carboxylic acid group ($-\text{COOH}$). The Glutamic acid monomer undergoes deprotonation to form carboxylate anion ($-\text{COO}^-$) and the amino group is oxidized to amino group radical cation. The interaction between these two ions results in the polymerization of Glutamic acid on the rGO electrode surface thus, leaving the remaining negatively charged carboxylate groups available for effective binding of the target moieties.^{35,36,38}

3.2 Characterization of the modified electrode

The surface morphology of the Poly-Glu/rGO electrode was characterized by SEM techniques. Figure 2a shows the rGO modified electrode portraying the distinct sheets of Graphene which indicates that GO on the electrode surface has been electrochemically reduced to rGO. Figure 2b shows the presence of Poly-Glutamic acid (Poly-Glu) over rGO, confirming that Glutamic acid has been successfully polymerized to Poly-Glu and it has grown regularly on the electrode surface.

The ATR-IR spectrum of Poly-Glu/rGO electrode is shown in Figure 3. The peaks located at around 1698 cm^{-1} and 1207 cm^{-1} correspond to the existence of $\text{N}-\text{H}$ and COO^- groups, indicating that the condensation might have taken place between the amino group of one glutamic acid and the carboxylate group of another one and the remaining COO^- group is retained in the

Figure 3. ATR-IR spectrum of Poly-Glu/rGO electrode surface.

monomer.³⁵ Additionally, the peaks around 1568 cm^{-1} and 2904 cm^{-1} were attributed to the $\text{C}=\text{C}$ stretching in the quinonoid ring and asymmetric stretching of $\text{C}-\text{H}$ bonds, corresponding to that of rGO.³⁹

Figure 4 depicts the typical AFM images of Poly-Glu/rGO electrode. The images confirm the random distribution of Glutamic acid polymers on the electrode surface. The root mean square value was found to be 16.245 nm. From this data, we can conclude that Poly-Glutamic acid was successfully homogeneously coated onto the surface of rGO. As expected, a high coverage uniform layer of Poly-Glutamic acid has been formed on the electrode surface with large surface roughness. Thus, the as-prepared Poly-Glu/rGO electrode is applicable for further electrocatalytic applications.^{40,41}

3.3 Analytical performance of the Poly-Glu/rGO electrode

3.3a Optimization of pH: Optimization of the electrochemical response of the modified electrode for

Figure 4. AFM images of Poly-Glu/rGO modified electrode surface.

Figure 5. Cyclic Voltammograms of the Poly-Glu/rGO modified electrode for the electrocatalytic oxidation of Gallic acid (7.0 μM) at various pH. Scan rate: 50 mV/s. Also shown are the (a) pH vs. Current and (b) pH vs. Potential plots.

Gallic acid was carried out. Figure 5 shows the current response for Poly-Glu/rGO electrode under varying conditions of pH (Scan rate: 50 mV/s). The influence of pH on the electrochemical oxidation of GA was studied in the range from 4.0 to 10.0. On increasing the pH from 4.0 to 5.0, an increase in the peak current was observed which diminished on further increase in the pH from 5.0 to 10.0, accompanied by a negative shift in the peak potential for GA oxidation as shown in the inset of Figure 5 (inset a). Thus, in order to achieve high oxidation current of GA, acetate buffer solution (ABS) at pH-5.0 was chosen for the further electrochemical determination of GA.

Figure 5(b) shows the plot of pH against oxidation of GA peak potential shift. The obtained linear equation is $E_{\text{pa}} (\text{V}) = (-0.05 \pm 0.021) \times + (0.59 \pm 0.03)$ ($R^2 = 0.998$). The relationship between pH and peak potential is given by equation (2).⁴²

$$\frac{dE_p}{dpH} = \frac{2.303mRT}{nF} \quad (2)$$

Here, m – number of protons, n – number of electrons, R – gas constant, T – temperature and F – Faraday constant. The ratio of the number of protons and electrons involved in the GA oxidation is 1:1. The number of electrons involved in the reaction has been calculated to be 2.

3.3b Optimization of Scan rate: The effect of scan rate (v) on the electrochemical responses of 5.0 μM Gallic acid at the Poly-Glu/rGO electrode in ABS-5.0 was also studied using cyclic voltammetry. The voltammograms were recorded at a scan rate of 10–500 mV/s. As shown in Figure 6, the oxidation current for GA increases with an increase in the scan rate. The oxidation peak currents for GA showed a linear relationship with the scan rate demonstrating a diffusion-controlled process. Furthermore, the plot of anodic peak currents (i_{pa}) as a function of square root of the scan rate and plot of peak potential as a function of scan rate (Figure 6a and b) in the range of 10 to 500 mV/s shows a linear relationship, with a linear regression coefficient

Figure 6. Effect of scan rate on the voltammogram for catalytic oxidation of 5.0 μM Gallic acid at Poly-Glu/rGO modified electrode in 0.1 M ABS at pH-5. (a) relationship between the square root of scan rate vs. current and (b) scan rate vs. potential plot.

Figure 7. Cyclic voltammograms of the PIGE (A and B) and Poly-Glu/rGO electrode (C and D) without and with 10 μM GA respectively; Scan rate: 50 mV/s, Supporting electrolyte 0.1 M ABS (pH-5).

(R^2) value of 0.988 and 0.992. The R^2 value of anodic peak currents (i_{pa}) vs. the square root of the scan rate is almost equal to the theoretical value of 1.0, which is generally expected for a diffusion-controlled redox system and thus confirms the above-mentioned result.⁴³

3.3c Electrochemical behavior of bare and modified electrodes: Figure 7 depicts the cyclic voltammograms for the unmodified PIGE electrode without GA (A) and in the presence of 10 μM GA (B). Here the current values observed for the electrocatalytic oxidation of Gallic acid was hardly noticeable when compared

Figure 8. Differential pulse voltammograms obtained with the Poly-Glu/rGO modified electrode for incremental addition of GA in 0.1 M ABS at pH-5 as supporting electrolyte and the corresponding calibration plot.

to the modified Poly-Glu/rGO electrode (C and D). At the modified electrode, distinct electrocatalytic behavior could be observed for a similar concentration of Gallic acid with enhanced anodic peak current values corresponding to the oxidation of Gallic acid at a potential of 0.5 V.

3.3d Electrochemical determination of Gallic Acid: Under optimized conditions, Differential Pulse Voltammetry (DPV) was employed for the electrochemical determination of GA using Poly-Glu/rGO electrode. Figure 8 illustrates the DPV response of Poly-Glu/rGO electrode with increasing concentrations of GA at a

Table 1. Comparison of the analytical performance of poly-Glu/rGO modified electrode towards GA determination with literature source.

Modified materials	Technique	Linear range (μM)	LOD (μM)	Ref
CPE@/CNT [#]	DPV	0.5–150	0.3	32
PEI ^{\$} -rGO/GCE	CV	0.58–58	0.41	33
PEP [%] /GCE	Ads DPV	1–20	0.66	34
Tyr [^] -nAu-GCE	Amperometry	25–900	7	35
TH [*] /NiHCF [!]	CV	4.99–120	1.66	36
Poly glu/rGO	Amperometry	1–17	0.53	Present
	DPV	0.03–480	0.0095	work

@– Carbon paste electrode.

\$– Polyethyleneimine.

– Carbon nanotubes

%– Polyepinephrine.

[^]– Tyrosinase.

*– Thionine.

!– Nickel hexacyanoferrate.

Figure 9. (a) Hydrodynamic voltammetric response of bare electrode (A and B) and Poly-Glu/rGO modified electrode (C and D) in the absence and presence of 110 μM GA, respectively, in 0.1 M acetate buffer at pH-5.0 under stirring condition of 300 rpm, scan rate:50 mV/s. (b) Chronoamperometric response of Poly-Glu/rGO modified the electrode on successive addition of GA in 0.1 M acetate buffer at pH-5.0 under the stirring condition of 300 rpm. Inset figure is the corresponding calibration plot.

potential window of -0.2 to 1.2 V. The electrocatalytic oxidation of GA was investigated in the concentration range of 0.03 – 480 μM with 0.1 M ABS-5.0 as the background electrolyte.

A sharp and well-defined peak was observed for the oxidation of GA and the peak current increased proportionally with increasing concentration of GA. The calibration plot of peak currents for the oxidation vs. GA concentrations was found to be linear in the concentration range of 0.03 – 480.0 μM (Figure 8 inset) with a linear regression coefficient value of (R^2) 0.999 and the detection limit was found to be 0.01 μM . The sensitivity of Poly-Glu/rGO electrode was found to be 0.97 $\mu\text{M}/\mu\text{A}$. The obtained linear range is larger than literature reports as shown in Table 1.^{44–48} This demonstrates the good electrocatalytic activity of the poly-Glu/rGO electrode for GA.

3.3e Determination of Gallic acid under dynamic conditions: In order to characterize the performance of Poly-Glu/rGO electrode for the determination of GA in flow systems and evaluate the influence of flow conditions on the catalytic oxidation of GA as a function of the applied potential, the hydrodynamic study was carried out. Figure 9a shows the hydrodynamic response of bare electrode (Curve A and B) in the presence of 110.0 μM of GA and Poly-Glu/rGO modified electrodes (Curve C and D) respectively in the presence of 110.0 μM of GA in 0.1 M ABS-5.0, at a scan rate 50 mV/s under stirring condition. It has been observed that the Poly-Glu/rGO electrode showed a good electrochemical response at 0.4 V for the catalytic oxidation of GA, whereas the bare and GO modified electrodes did not show any considerable current response under similar conditions. The rGO electrode favored GA oxidation

at very low potential however, the sensitivity was poor. The electrocatalytic activity of Poly-Glu/rGO surface permitted convenient determination of GA with high sensitivity. Thus, a potential of 0.4 V was fixed for the amperometric studies.

3.3f Amperometric determination of GA: The amperometric response of Poly-Glu/rGO electrode towards the electrocatalytic oxidation of GA was analyzed by carrying out the analysis under stirring conditions. The maximum potential value of 0.4 V obtained from the hydrodynamic studies was fixed for the amperometric determination of GA in 0.1 M ABS-5.0. Figure 9b shows the amperometric response of GA in the concentration range of 1.0–17.0 μM . Here the concentration range was much reduced compared to the differential pulse voltammetric response (section 3.3c) with the modified electrode. This may be due to the mass transfer of the analyte towards the surface under stirring conditions. Each step-wise addition of GA was accompanied by a sharp increase in the current. The electrode also showed a fast response time of about 3 s. The inset calibration plot represents the linear relationship between the catalytic current and GA concentration. The rapid electrochemical response of Poly-Glu/rGO electrode towards the electrocatalytic oxidation of GA reveals its viable application as a potent electrochemical sensor in flow systems.

3.4 Interference studies

The effect of various interfering species on the determination of GA using Poly-Glu/rGO electrode was examined in order to assess its possible analytical applications. The selectivity of the sensor in the presence of range of compounds including polyphenols and neurotransmitters (catechol (CC), hydroquinone (HQ), resorcinol (RC), dopamine (DA), ascorbic acid (AA), uric acid (UA) and catechin (CT) were studied since these compounds have an oxidation potential very close to that of GA.⁴⁹ The interference studies were carried out by recording the current response of GA in the presence of equal or excess concentration of the interfering species. The Poly-Glu/rGO electrode showed no considerable deviations in the current response of GA in the presence of CC, HQ, RC, CT and AA ions. However, the results as shown in Figure 10 indicate that UA and DA could be oxidized at the modified electrode but the potentials were far away from that of GA at 0.17 V and 0.85 V respectively. Also, there was no considerable increase in the oxidation current on further additions of UA and DA. Hence, the oxidation of GA in presence of UA and DA could be carried out without any considerable interference. The electrode modification

Figure 10. DPV plot of Poly-Glu/rGO electrode in 0.1 M ABS (pH-5) containing 300 μM GA, 600 μM UA and 600 μM DA.

Figure 11. Storage stability of Poly-Glu/rGO electrode over a period of 60 days.

protocol thus provides for strong interactions with GA favouring its selective detection.

3.5 Stability and reproducibility Poly-Glu/rGO electrode

The modified electrode was placed in acetate buffer (ABS-5) once the experiment is complete and scanned until the GA oxidation peak disappears. The modified electrode was utilized to study the percentage of change in oxidation current of GA over a period of 4 weeks and the current changes were monitored. A small decrease in current was observed over this period (less than 1% (± 0.001) from initial current). Although the current response decreased gradually on

Table 2. Determination of GA in green tea samples using poly-Glu/rGO modified electrode.

Sample ID	Added (μM)	Found (μM)	Recovery (%)	RSD (%)*
I	5	5.2 (± 0.02)	104	2.36
	15	15.08 (± 0.01)	100.5	1.89
II	7	6.8 (± 0.03)	97.1	1.98
	20	20.1 (± 0.025)	100.5	2.35

*RSD reported for three parallel determinations (n=3).

storage, it retained almost 95% of its initial response after 2 months (Figure 11). This indicates that the rGO/Poly-Glu electrode is suitable for long-term applications. The electrode was stored in a refrigerator at 4 °C when not in use.

3.6 Real sample analysis

The modified electrode was employed for the estimation of GA in two different brands of green tea samples by the voltammetric method under optimized conditions. The green tea samples were purchased from the local markets. The tea samples were extracted by a simple filtration method. About 100 mg of dried and powered green tea leaves were transferred to 20 mL of double distilled water followed by boiling at 80 °C for 15 min then allowed to cool at room temperature. The extract was filtered using Whatman 42 filter paper and transferred to a 100 mL flask and diluted with double distilled water. This sample was further subjected to electrochemical analysis by standard addition method. The accuracy of this method expressed in terms of recoveries indicate that the proposed system proves efficient for the quantitation of GA in the green tea samples. The recovery range including the RSD for three parallel determinations is listed in Table 2. The observed recovery percentages of GA obtained in the samples taken were found to be satisfactory.

4. Conclusions

In summary, a simple electrochemical platform for fast, sensitive and selective determination of GA has been developed successfully. The sensor showed a good linear response in the range of 0.03 μM to 480 μM with a detection limit of 0.01 μM . The as-developed sensor showed good potential for the determination of GA in commercial tea samples. Therefore, a simple and reliable strategy has been proposed for fabricating Poly-Glu/rGO modified electrode with great potential for use as an electrochemical sensor for the determination of GA.

Acknowledgements

The authors gratefully acknowledge the support of this work by DST-SERB, New Delhi, India.

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