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Ultrasensitive Quantification of Ellagic Acid using Gr/Bi₂O₃/GCE as Voltammetric Sensor

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A simple and sensitive voltammetric sensor Gr/Bi₂O₃/GCE is being reported for the quantification of Ellagic acid (EA). The developed sensor was characterized by Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX), Electrochemical Impedance (EI), Fourier Transformed Infrared (FTIR) and X-Ray Diffraction (XRD). The Electrochemical measurements were performed using square wave and cyclic voltammetry. The fabricated sensor exhibits an excellent catalytic response towards the oxidation of EA with a well-defined oxidation peak at 0.6 V in Britton Robinson buffer at pH 3.0. Variation in the peak response through solution variables viz. pH and amount of analyte has also been studied. The fabricated sensor depicted an excellent linear calibration curve for EA with sensitivity of 0.07 nM. The fabricated sensor is proficient to quantify EA effectively without any interference. The analytical application of the sensor has been authenticated by quantifying the EA in real samples.

Keywords: Ellagic acid; Glassy Carbon Electrode; Electrochemical Impedance Spectroscopy

1. INTRODUCTION

Polyphenols derived from plants play significant role in human nutrition and possess numerous biological properties including antioxidant, anti-inflammatory, anticancer and antiatherosclerotic activities. Ellagic acid (EA) is a fused four-ring polyphenol dimeric imitative of gallic acid and found in various fruits and vegetables including strawberries, raspberries, pomegranate (Quercusrobur, Quercus alba), walnut trees (Junglansnigra) and chestnut trees (Castanea sativa) in the form glycosides or linked in the ellagitannin structures and but little amount may present as free acid in plants [1-5]. In various cases EA has also been used as dietary supplement with high benefits against cancer and heart diseases. It is also well known as food additives, as it has antioxidative and antiviral property [6-12]. Different techniques have been reported for its quantification in foodstuff, such as chromatography spectrophotometry and capillary electrophoresis [13-18]. Due to the limitation of these techniques such

as poor accuracy or the need for expensive instrumentation with high operating costs, in recent years, advances in the development of new electrochemical sensor for electrochemical quantification of EA has received considerable interests. Electrochemical techniques are often applied rather than above techniques because of their high selectivity, low detection limit, cost effectiveness and they require less time consuming sample preparation setup. Chemically modified electrodes have been frequently applied as sensitive and selective analytical tools for EA analysis [19-22]. A wide range of nanomaterials of unique chemical, physical and electronic properties, owing to their small size, nanomaterials are gaining considerable interest as electrochemical sensor. Among these, metal oxide based sensor are found to exhibit higher electrocatalytic activity, stability and reproducibility for the quantification of different analyte over unmodified (bare) electrode [23-25]. In the present study Gr/Bi₂O₃ based electrochemical sensing platform has been fruitfully applied to quantify lowest the concentration of EA in different real samples. To the best of our knowledge, so far no voltammetric study is available at Gr/Bi₂O₃/GC sensor.

2. EXPERIMENTAL

2.1. Reagents and Chemicals

Ellagic acid (EA) (\geq 98%) was procured from TCI chemicals and used as received. Graphite nanopowder (Gr), bismuth (III) oxide (Bi₂O₃) and all the other reagents were purchased from Sigma Aldrich and used without further purification. All solutions were prepared in Milli Q water. With the aid of ultrsonication, stock solutions of analyte was prepared by dissolving suitable amount of analyte in methanol and kept in refrigerator at 4^oC. Further working solutions of analyte were freshly prepared by diluting stock solution of different concentrations by mixing with methanol.

2.2. Instrumentation

AUTOLAB 112 Potentiostategalvanostate 302 N (the Netherlands) with software NOVA 1.1 was applied for all the voltammetric and impedance measurements respectively, with a conventional three-electrode system , a GCE (diameter = 3.0 mm) as working electrode, platinum electrode as auxillary electrod, and Ag/AgCl (saturated 3.0 M KCl) as reference electrodes, respectively. The pH measurements were made using Decible DB-1011 digital pH meter. Electrochemical impedance measurements were done in 0.1 M KCl solution containing 3 mM K₃[Fe(CN)₆].

2.3. Preparation of the Graphite/Bismuth Oxide /Glassy Carbon Sensor (Gr/Bi₂O₃/GC Sensor)

The GCE was polished before the experiment with slurries of alumina powder on microcloth polishing kit, until the appearance of mirror like surface and rinsed thoroughly with distilled water. After subsequently cleaning electrode was sonicated in ethanol, followed by distilled water for about

15 s and then dried at room temperature. For the development of $Gr/Bi_2O_3/GC$ Sensor, 1.0 mg Graphite nanopowder and 1.0 mg Bi_2O_3 were dispersed in 1.0 mL of dimethylformamide, followed by ultasonication for 1 h. Finally $Gr/Bi_2O_3/GC$ sensor was prepared by drop casting method. Four microliters of prepared above suspension was dropped on the clean surface of GCE and dried in air at room temperature.

2.4. Voltammetric procedures

Square Wave Voltammetric technique was applied for the quantification of EA at following optimized parameters: equilibration time: 5 s, frequency: 10 Hz, amplitude: 50 mV. The voltammograms were recorded by scanning the potential between 0.0 to 1.0 V cyclic voltammetric studies were carried for studying the reversibility of analyte.

3. RESULTS AND DISCUSSION

3.1. Characterization of developed Gr/Bi₂O₃/GC sensor

3.1.1. Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX)

In order to check, whether the dispersion of bismuth (III) oxide in graphite resulted in any modification in the topography of fabricated sensor surface, the morphological study of Bi_2O_3 , Gr and Gr/Bi_2O_3 were studied using SEM and images have been depicted in Fig.1. From Fig. 1 (A)-(C), it is clear that bismuth (III) oxide, in the matrix of graphite forming honeybee comb like structure and uniformly dispersed, providing a greater electroactive surface, as compared to graphite, which enhance the electron transfer during the electrode process.



[B]



Figure 1. Scanning electron microscopic images of (A) Graphite (B) Bismuth (III) oxide (C) Gr/Bi₂O₃

3.1.2. X- ray diffraction (XRD)

Formation of honey bee comb shape nanoparticles of graphite-bismuth oxide confirmed with sharp intense and well defined X ray pattern. The XRD analysis of graphite-bismuth oxide (Figure 2 C) shows the typical peaks at 2θ equal to 27^{0} , 30^{0} , 32^{0} , 48^{0} , 58^{0} , 59^{0} and 78^{0} . These peaks are present in (Figure 2 A & B) almost at same 2θ [35].





Figure 2. XRD pattern of (A) Bismth (III) oxide (B) Graphite (C) Graphite- Bismth (III) oxide

3.1.3. Energy dispersive X-ray spectroscopy (EDX)

The qualitative and quantitative confirmation of nanocomposite can be done by EDX analysis. From the spectra, (Figure 3 A-C), it can be clearly seen that the peaks are corresponding to bismuth, carbon and oxygen, which show there are no additional impurities or interferences. The weight % contributions of various elements in formation of noble nanocomposite are as follow, Bismuth-42%, Carbon-48% and Oxygen-10%.



Figure 3. EDX spectra of (A) Bi_2O_3 (B) Gr (C) Gr/Bi_2O_3 (D) Plot of elemental composition vs weight %

3.1.4. Fourier Transform Infrared Spectroscopy (FTIR)

IR peaks assigned at 3506.20 cm⁻¹ for O-H moieties, O=Bi at 522.40 cm⁻¹ and C=C moieties at 1656.69 cm⁻¹ and C=O at 1590.54 cm⁻¹ (Figure 4 C) in nanocomposite. The band near 1595 cm⁻¹ due to C=C and 1787.53 cm⁻¹ due to C=O (Figure B) and O=Bi at 522.77 cm⁻¹ (Figure A). All the peaks are present in Gr/Bi₂O₃ nanocomposite which confirms the formation of Gr-Bi₂O₃ nanocomposite [36].



Figure 4. Infrared spectrum of (A) Bi₂O₃ (B) Graphite (C) Gr/Bi₂O₃

3.1.5. Electrochemical Impedance Spectroscopy (EIS)

The dielectric properties of a sensor can be detected by electrochemical impedance technique over a range of frequencies. The Nyquist plot (impedance spectrum) incorporated with range of frequency. The higher frequency with more semicircle part corresponding to the electron transfer limited process and frequency ranges with lower semicircle arc corresponding to the diffusion limited process. The dielectric and insulating features at the electrode/electrolyte interface plays a major role in charge transfer resistance (Rct) of modified sensor [26-28]. The interface properties of modified electrodes were characterized by recording EI spectra in redox probe media i.e. 3.0 mM solution of K_3 [Fe(CN)₆]. Figure 5 indicates the Nyquist plots of electrochemical impedance spectrum in Phosphate Buffer of pH 7.



Figure 5. EIS spectra of (a) bare GC (b) Bi₂O₃/GC (c) Gr/ Bi₂O₃/GC sensor in 3.0 mM K₃[Fe(CN)₆] prepared in phosphate buffer pH 7.0

Figure 5 (Nyquist plots), illustrate that the Rct values of modified sensors decreases to lower value in comparison to the bare. From the figure, we conclude that, after the fabrication, there is a decrement in Rct value, with the enhanced surface area of the modified surface that eases the charge transfer and caused in decrease in Rct. The Rct value was observed to be decreases from 99 k Ω for Bare GCE, to 33.3 k Ω for Bi₂O₃/GC and 13.2 k Ω for Gr/Bi₂O₃/GC sensor, which clearly indicates better electrocatalytic effect of developed sensor.

3.1.6. Surface area study

The electrochemical characterization of bare and fabricated sensors were carried out by applying $K_3[Fe(CN)_6]$ using CV technique. In order to illustrate, the effects of Gr and Bi₂O₃ on the electrode surface, CVs for 1.0 mM of $K_3[Fe(CN)_6]$ in PBS pH 7.0 at the bare and fabricated sensors were recorded (Figure 6). Recorded signals (Figure 6), at the Gr/Bi₂O₃/GC sensor showed better response due to enhanced conductivity and improved electrocatalytic properties. The active surface area of developed sensor was calculated from the Randles-Sevcik equation (eq.i) for irreversible diffusion-controlled process [34].

Here, for $K_3[Fe(CN)_6]$ the values of n and D are 1 and 7.6 x 10⁻⁶ cm² s⁻¹ respectively and the surface area of bare and fabricated sensors were calculated from the obtained slope of I vs $v^{1/2}$.

CVs were recorded at different scan rates (from 10 to 100 mV s⁻¹) which indicated linear relationships between the cathodic peak current and the square root of the scan rate. The active area for bare was 0.023 cm², Bi₂O₃/GCE was 0.037 cm² while Gr/Bi₂O₃/GCE presented an active surface area of 0.048 cm². These values revealed that the surface modification increased the electrochemical effective surface area by twice the value of bare GCE.



Figure 6. Cyclic voltammograms of 1.0 mM K₃[Fe(CN)₆] in 1.0 M KCl solution at pH 7.0 Bare GC (Black), Bi₂O₃/GC (Green) and Gr/Bi₂O₃/CG sensor (Pink).

3.2. Performance of EA at the fabricated Sensors

For all electrochemical measurements, 18mL of BR buffer (pH 3.0) was added into the electrochemical cell in which the bare or fabricated GCE was immersed. An aliquot of the working solution was added to the electrochemical cell at optimized instrumental conditions. The solution was set to equilibrate for 10 s subsequent to sweeping from 0.0 to 1.0 V. Ellagic acid (2.5nM) at pH 3.0 at bare GCE, Bi₂O₃/GCE and Gr/Bi₂O₃/GCE under optimized conditions gave well-defined anodic peak (Figure 7). An enhancement of 10 times in peak current was recorded at Gr/Bi₂O₃/GC sensor compared to bare GCE and Bi₂O₃/GCE (Curve a, b and c respectively) with slight shift in peak potential. Increased sensitivity of developed sensor is also supported by the reduction in the RCT values of fabricated sensors as observed EIS studies.



Figure 7. Square Wave Voltammograms of 2.5 nM solution of EA at different sensors (a) Bare (red) (b) Bi₂O₃/GC (green) (c) Gr/Bi₂O₃/GC (blue) at BR buffer 3.0 pH

Electrochemical behaviors of EA were studied in various buffers such as BR, phosphate and acetate buffers at bare and fabricated sensors. Maximum peak current response was observed in universal BR buffer. Thus, for all measurements, BR-buffer was selected. The peak current and potential was affected on going from acidic to basic medium. On going from more acidic to less acidic medium peak current increased up to pH 3.0. After that peak current decreases slightly on going towards more basic. Slight shifting in Peak potential was observed towards less positive value on moving towards acidic to basic medium. Best peak current was observed at pH 3.0 so it was optimized for the further experiment (Figure 8). This process is associated to the proton participation in electrode reaction. The observed slope value of the linear equation is found to be 0.067 mV that is closest to the Nernstian value of 0.059 mV at ideal room temperature and pressure. The obtained result demonstrated that equal number of proton and electron transfer in electrode process. The m/n ratio also evident the equal number of proton and electron transfer. Linear dependency of peak potential on pH can be predicted from the equation (ii)

EA:
$$y = 0.067x + 0.810$$
 R²=0.992 (ii)



Figure 8. Plot of Effect of pH on (A) Peak current (B) Peak potential

3.3. Cyclic Voltammetry

To confirm the irreversibility of EA, electrocatalytic behaviour of 9 μ M EA was examined in the potential range of 1.0 V to -0.3V. A well defined oxidation peak was observed on initiating in positive direction while no reduction peak was found in reverse scan, which confirmed the irreversible nature of the electrode process, which is in good agreement with earlier reported methods [19, 21]. The effect of scan rate on peak current and peak potential has been represented in Figure 9 A-C, which shows that peak current rose linearly on increasing scan rate from 10 mV s⁻¹to 100 mV s⁻¹.

From the figure it is evidently observed that there is an absence of reduction peak in reverse scan of CV. On potting the calibration graph between log ip and log scan rate, the achieved slope value is 0.59 confirmed the diffusion controlled nature of the electrode process.

EA:
$$i_p=0.598x+0.045$$
, $R^2=0.999$ (v)

To confirm the irreversible diffusion controlled electrode phenomena, a calibration graph is plotted between Ep and logarithm of v and compared with the equation discussed below

$$Ep=E0 + (RT/\alpha naF) [0.78 + \ln (D0 1/2/K0) + \ln (\alpha naF v/RT)1/2]$$
(vi)

In this study on plotting a graph it is observed that Ep linearly depends on $\ln v$ according to equations (vii).

EA,
$$Ep = -0.058x + 0.362$$
 ($R^2 = 0.983$) (vii)

From above equations (6) & (7) we can obtain that

EA,
$$(RT/\alpha naF) = 0.058$$
 (v)

Here R, T, F has their standard meaning and by keeping these values in above equations number of electrons (n) were calculated n=1 [34].



Figure 9. (A) Plot of I versus $\upsilon^{1/2}$ (B) Plot of log I vs log of υ (C) Plot of ln υ vs Ep (D) Cyclic voltammograms of EA (9 μ M) at different scan rates (υ) (a) 10 mV s⁻¹ (b) 25 mV s⁻¹ (c) 50 mV s⁻¹ (d) 75 mV s⁻¹ (e) 100 mV s⁻¹ in BR buffer pH 3.0

3.4. Optimization of other operational parameters

In order to obtain the finest voltammetric response of EA, casting volume of nanocomposite on the electrode surface was tested and optimized. On increasing volume of prepared nanocomposite from 1-5 μ L on the surface of electrode, there was an increase in the whole conductivity upto 4 μ L as the effective surface area increased, afterwards peak current decreases on increasing the volume. So, 4 μ L volume was selected for further experiments (Figure 10 A). Relative voltammetric response of EA in various solvents viz. methanol, ethanol, DMF and different surfactants viz. SLS, triton-X100, CTAB,



were examined and maximum current response was in methanol (Figure 10 B).

Figure 10. Plot of (A) Different volumes of Gr/Bi₂O₃ vs Current (B) Different solvents vs current

3.5. Method Validation

3.5.1. Calibration curve

Under the optimized parameters square wave voltammetric technique was applied for the quantification of EA, where, a sharp oxidation peak was observed with higher sensitivity and selectivity (Figure 11). Oxidation peak current increased linearly with increased in concentration of EA and the detection limit was 0.07 nM and limit of quantification 0.21 nM. The LOD and LOQ were calculated using the formula: LOD= 3s/b and LOQ= 10s/b, where s is the standard deviation of the peak response and b is the slope of the calibration curve. A comparative table of the analytical performance of Gr/Bi₂O₃/GC sensor with other fabricated electrochemical sensor for EA quantification has been summarized in Table 1. From the table it can be safely concluded that the developed sensor possess higher sensitivity with low detection limit, which can be attributed to the synergistic effect of Gr/Bi₂O₃ with increased surface area and better conductivity. The fabricated sensor demonstrated good reproducibility where relative standard deviation (RSD) was less than 5% which also confirmed the good stability of the fabricated sensor.



Figure 11. Square wave voltammograms at Gr/Bi₂O₃/GC sensor in BR buffer (pH 3.0) in the concentration range of (a) Blank (b) 0.5 (c) 1.0 (d) 1.5 (e) 2.0 (f) 2.5 (g) 3.0 (h) 3.5 nM

3.5.2 Sensor Application

Applicability of proposed method was evaluated by the recovery of EA in real samples from walnut and pomegranate. Experiments were performed in pre optimized condition on developed sensor by standard addition method. The recovery of EA was investigated by SWV technique. Five replicates were recorded using 5 different concentrations of EA (Figure 12). Good recovery could be achieved in the range of 99.0%-101.5% which signifies the appropriateness of the fabricated sensor. A small quantity of walnut (1.0 g) was weighed and grinded, followed by the addition of 10 mL of methanol into the sample and mixed for 1 h and EA was extracted with help of Soxhlet assembly. After that, remaining liquid part was separated and diluted to 25 mL with methanol. The flask A was diluted with methnol up to the mark.0.02 mM standard solution of EA was added as 100,200,300,400µL in labeled flask from B to E. The flasks were diluted up to the mark with methanol. After that current response was examined for every sample and graph plotted between analyte concentration and current response in Y-axis. To quantify analyte concentration in real sample linear regression analyses was carried out and slope (m) and intercept (b) were evaluated. Unknown amount of target molecule was quantified by using following equation (ix),

Cx = b.Cs/m.Vx(ix)

Cx =Concentration of the sample, Cs =Concentration of the standard, Vx = Volume of the sample aliquot, m = Slope of linear regression, b = Intercept of linear regression.

On the basis of above equation by substituting the value of "b" & "m" from regression equation (y = 0.008 + 1.474), Cs = $0.6 \mu g/mL$, Vx = 2 mL, concentration of EA in real sample was found to be $0.32 \mu g/mL$.

Table 1. Concentration of EA in extract of walnut and pomegranate

Sample	EA μg/mL
Walnut	0.032
Pomegranate	0.040



Figure 12. Square wave voltammograms at Gr/Bi₂O₃/GC sensor for determination of EA by standard addition method in walnut in BR buffer (pH 3.0) (a) blank (b) sample (c) 0.06 μ g/mL (d) 0.12 μ g/mL (e) 0.18 μ g/mL (f) 0.24 μ g/mL of standard E

3.5.3. Interference Study

Under the optimized experimental conditions, the selectivity of the sensor was evaluated. The peak response can be considerably changes in the presence of few interfering materials. So interference of various substance viz. inorganic ions (Na⁺,K⁺,Ca²⁺Cl⁻, SO₄²⁻, CO₃²⁻), Glucose, Fructose, Eugenol, Capscasin as compounds, was examined because they are mostly there in biological samples. The tolerance limit error was found to be less than 5% in the quantification of 10 mM EA. No interference could be observed by this compound.

3.5.4. Comparison with earlier reported techniques

This is the first systematic report of electrochemical oxidation of ellagic acid. Previously reported studies have shown the redox nature of EA towards developed sensor [31-32]. Various voltammetric experiments were carried out using square wave and cyclic voltammetry, despite of all the experiments, a reduction cannot be identified and electron transfer process is diffusion controlled [30]. The corresponding voltammograms are shown in (Figure 7, 9(d) and 11), from (Fig.9 d) we can conclude the irreversibility of EA towards developed sensor [21].

As compare to other reported methods (Table.2) and developed sensors, this sensor has shown good recovery, reproducibility, stability and LOD.

S.No.	Sensor	LOD (nM)	Reference
1.	PIGE/GCE	130	29
2.	CPE/MWNT	0.21	30
3.	GCE	10	31
4.	SPE-GPH	40000	32
5.	Gr/Bi ₂ O ₃ /GCE	0.07	Present Work

Table 2. Comparative study of the previously reported results with the proposed method

4. CONCLUSION

In this study, a sensitive and selective voltammetric sensor based on a glassy carbon electrode modified with graphite/bismuth (III) oxide has been developed. The fabricated sensor was applied for the voltammetric quantification of EA. The developed sensor efficiently ease both the diffusion of EA to the surface of electrode and the electron transfer of EA molecules, hence enhancing the sensitivity of the fabricated electrode over bare. The proposed method was appropriated to quantify the EA in different real samples with a good recovery of 99.5 %. This is the first systematic report for determination EA at Gr/Bi₂O₃/GCE based sensor. Various characterization techniques such as SEM-EDX, FTIR, XRD, CV and EIS were applied to characterize the developed sensor. The developed sensor was found to be highly sensitive, lower detection limit and having good reproducibility and repeatability.

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