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2019

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Zinc oxide nanoparticles modified-carbon paste electrode used for the electrochemical determination of Gallic acid

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Abstract. Zinc oxide nanoparticles (nano-ZnO) was used to modify carbon paste electrode (CPE) for a fast and sensitive electrochemical determination of gallic acid (GA). The study was carried out using cyclic voltammetry (CV and differential voltammetry (DPV) techniques, where the nano-ZnO-modified electrode exhibited an efficient and sensitive oxidation of GA. The cyclic voltammetric result showed a significant enhancement of the peak current from 250µA to about 410µA. The electrochemical behaviour of GA on the nano-ZnO modified carbon paste electrode was studied using DPV, showing a sensitivity of the electrode in a concentration range of 1 x 10^{-6} to 5.0 x 10^{-5} mol L^{-1}, with a correlation coefficient R^2 of 0.9968 and a limit of detection of 1.86 x 10^{-7} mol L^{-1} (S/N =3). The proposed electrode was used successfully for the determination of GA in red wine with recoveries of 103%.

Keywords: Zinc oxide nanoparticles, Gallic acid, cyclic voltammetry, differential pulse voltammetry, electrochemistry

1. Introduction

The use of nanomaterials for the development of electrochemical sensors have attracted considerable interest because of their special chemical and physical properties [1]. Their versatile nature of ZnO nanoparticles (nano-ZnO) in metal oxide nanoparticles development, has led to their use in different applications like solar cell, photocatalytic activity, and as chemical and biological sensors [2]. The high surface area to volume ratio, high thermal, mechanical and chemical stability are advantages that has made them useful in sensors and electrode modification [3].

Carbon paste electrodes (CPEs) are heterogeneous binary mixtures of graphite and organic liquid (Paraffin oil) with no electrolytic character. They have been used as sensitive and selective sensors for electrochemical applications, because of their very low background current, broad potential range, low cost, ease of preparation, very simple renewal of the surface and their ease to miniaturize [4].

Gallic acid (2,3,4-trihydroxybenzoic acid) (GA) is a naturally occurring phenolic compound found in plants, tea, fruits, wine and also functions as a natural antioxidant, with several biological activities. Studies have shown their anti-carcinogenic, anti-mutagenic and anti-oxidative properties [5]; hence their importance in diseases like Alzheimer's, Parkinson's, diabetes, cancer and cardiovascular diseases [6]. The antioxidant capacity of GA has been mainly studied by spectrophotometric methods, chromatographic and electrochemical methods [7]. However, some of the main drawbacks have been the cost of equipment, extensive time-consuming sample preparation processes and the use of toxic

reagents that can be detrimental to the environment. Electrochemical methods have the advantage of being fast, sensitive, inexpensive and portable.

Different ZnO nanoparticles composites and combinations have previously been used for carbon paste modification in the determination of naproxen [2] levodopa in the presence of ascorbic acid [3]. However, there hasn't been any used for the determination of GA. Nanomaterials such as SiO_2 and TiO_2 have been previously employed in the modification of carbon paste electrodes for the determination of GA [8]. However, selectivity and extensive time consumption in electrode preparation were the main drawbacks.

In this work for the first time ZnO nanoparticles synthesized using the solochemical method have been used for the determination of GA in combination with carbon paste. The modified carbon paste electrode was also used for the successful determination of GA in red wine.

2. Experimental procedure

2.1. Reagents and Materials
Gallic acid (anhydrous, molar mass 170.12 g mol^{-1}), Zinc nitrate hexahydrate (molar mass 180.36 g mol^{-1}), sodium hydroxide pellets and graphite powder were purchased from Sigma Aldrich (London, UK). All the reagents unless stated were of the highest purity; with no further purification required. All the electrochemical and the electrochemical impedance spectroscopy (EIS) measurements were performed using an Ivium Vertex One potentiostat-galvanostat, with analysis done with Iviumsoft software (Eindhoven, Netherland). The standard three-electrode system was employed, that consisted of the ZnO nanoparticles modified-CPE as working electrode, a KCl saturated Ag/AgCl reference electrode and a platinum wire counter electrode (auxiliary electrode) from BASi (West Lafayette, USA).

2.2. Synthesis of ZnO nanoparticles and Modification of Carbon Paste Electrode
ZnO nanoparticles was synthesised using a synthesis procedure developed by Gusatti *et al.* [9] which consisted of dissolving about 12g of $Zn(NO_3)_2.6H_2O$ in 100 mL deionized water in a beaker and then stirred for 25mins using a magnetic stirrer. The resulting solution was heated while being constantly stirred up to a temperature of 70°C. Subsequently about 3.2g of NaOH was dissolved into 30 mL of deionized water in a sperate beaker and stirred for about 10 mins. After this, the solution of NaOH was slowly added drop-wise into the $Zn(NO_3)_2.6H_2O$ solution under continuous stirring. The suspension that is formed with the addition of the NaOH alkaline aqueous solution into the $Zn(NO_3)_2.6H_2O$ solution was kept at 70°C for 2hrs under constant stirring. The mixed solution was then left to settle at normal air condition for few hours and filtered using a Whatman filter paper. The filtered sample was dried in oven at 65°C for 24hrs.

The carbon paste electrode was prepared by hand mixing of graphite powder with paraffin at a ratio of 60:30 (w/w) in an agate mortar. The amounts of ZnO nanoparticles was 10%, for the modified carbon paste electrode. The paste was then inserted into a Teflon tube of 2mm internal radius and smoothed using a weighing paper. Electrical connection was made by connecting a copper wire into the tube. The face of the electrode was renewed by polishing it on filter paper.

3. Results and discussion
The ZnO nanoparticles were characterised using SEM, EDXA and FTIR as can be seen in Figure 1. The SEM image shows quasi-spherical structures of the ZnO nanoparticles (Figure 1a) and the nano-ZnO-CPE (Figure 1b) showing the homogenized ZnO nanoparticles-graphite powder in the carbon paste. Meanwhile the EDXA data in (Figure 1c) shows the elemental composition of the ZnO nanoparticles made up of Zinc and Oxygen molecules. The FTIR image in Figure 1d shows a typical spectrum for ZnO nanoparticles, where the peak found mainly between 500-400 cm^{-1} is a typical peak for Zn-O bond absorption and the broad absorption peak found around 3300 – 3500 cm^{-1} could be attributed to the characteristic hydroxyl bond absorption. The FTIR data are similar to other data obtained by others [10] in the literature.
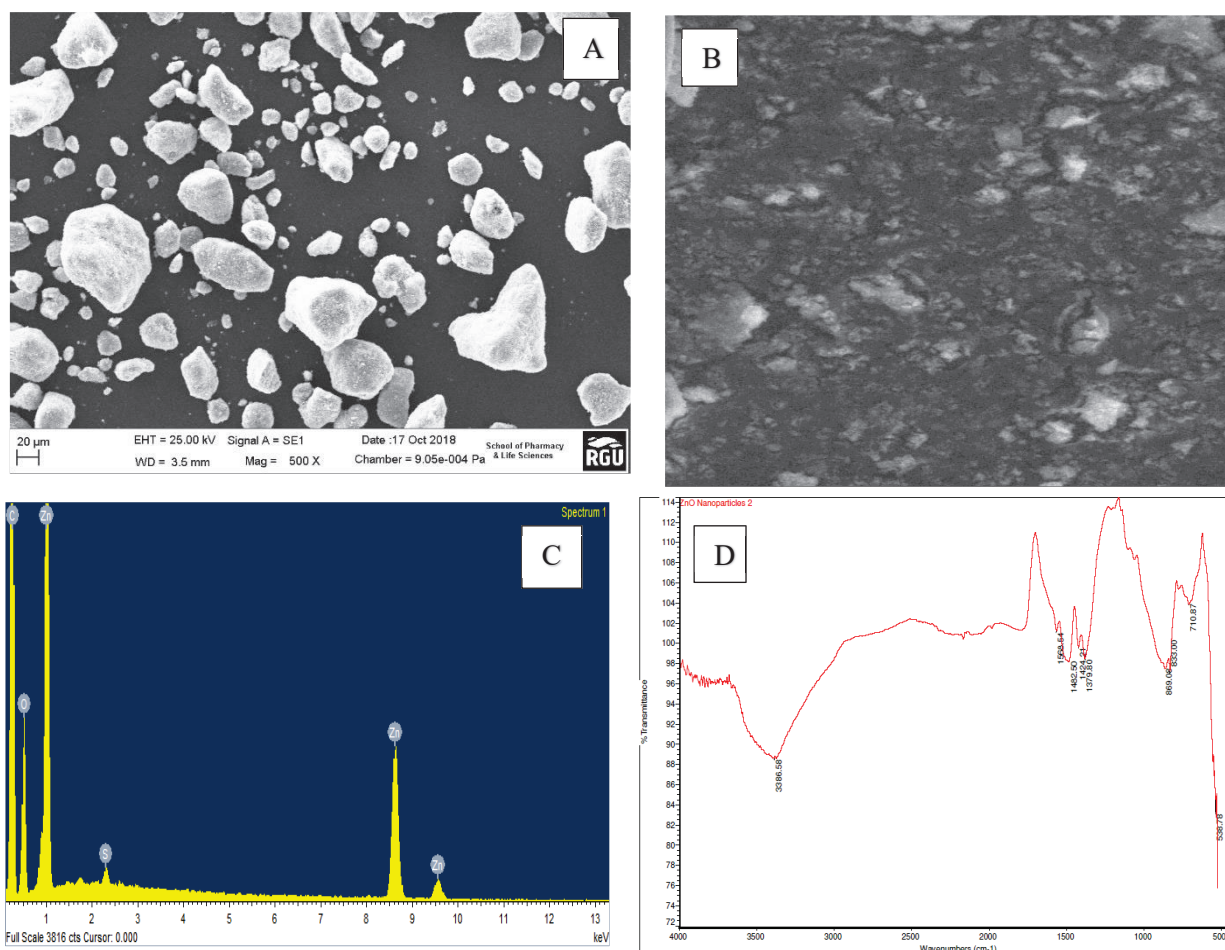
Figure 1. (a) SEM image of ZnO nanoparticles (b) SEM image of ZnO-nanoparticles homogenized in the carbon paste electrode (c) The EDXA analysis of the synthesised compound showing its composition of Zinc and Oxygen (d) FT-IR spectra of ZnO nanoparticles

Cyclic voltammetry was used to study the electrochemical interaction between GA and the ZnO nanoparticles modified CPE. Figure 2 shows cyclic voltammograms of ZnO nanoparticles-CPE and bare CPE, in a 0.1 mol L^{-1} phosphate buffer solution (PBS, pH 2.0) containing 1 x 10^{-1} mmol L^{-1} GA at a scan rate of 100mV s^{-1}, through an applied potential range of 0-1.8V. It was observed that, the nano-ZnO-CPE improved the oxidation current or peak current from about 250µA for the bare-CPE to 410µA for the modified electrode. However, the peak potential did not show any negative shift from the bare-CPE to the nano-ZnO-CPE, instead there was a slight positive shift of about 0.03V. There was an enhancement of the peak current (Ip), because of the increased surface to volume ratio of the ZnO nanoparticles from about 0.063cm^2 to 0.188cm^2.
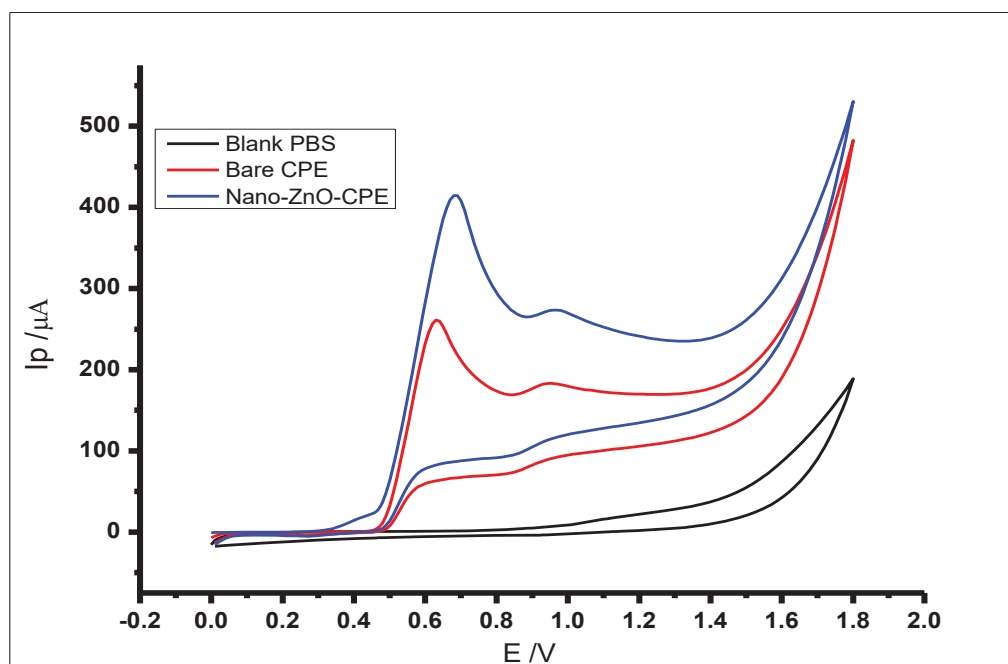
Figure 2. Voltammograms of 1 x 10^{-2} mol L^{-1} Gallic acid in a 0.1 mol L^{-2} PBS buffer at pH 2.0, determined using a carbon paste electrode and a ZnO nanoparticles modified carbon paste electrode using Cyclic Voltammetry, at a scan rate of 100mV/s at room temperature.

The electrochemical performance of the ZnO-nanoparticles-CPE as compared to the bare CPE was studied using electrochemical impedance spectroscopy and CV in a 1 x 10^{-3} mol L^{-1} $K_3Fe(CN)_6$ – $K_4Fe(CN)_6$, where the voltammograms were used to calculate the active surface area of the electrode (Figure 3). From the data produced the electroactive surface area was determined using the Randles-Ševčík equation for a reversible process, with a diffusion coefficient of 7.6 x 10^{-6} cm^2 s^{-1} for $[Fe(CN)_6]^{3-}$ and n=1.

$$I_{pa} = (2.69 \ x \ 10^5) n^{2/3} A \ D^{1/2} \ \gamma^{1/2} C_o \qquad (1)$$

Where n is the number of electrons transferred, A is the electroactive area of the electrode, D is the diffusion coefficient, γ is the scan rate and C the concentration of the redox probe used. The electroactive surface areas were calculated from plots of Ip vs $\gamma^{1/2}$ (square root of scan rate), having slopes of 0.1416 x 10^{-4} A $\gamma^{-1/2}$ $D^{1/2}$ for the nano-ZnO-CPE and 0.0471 x 10^{-4} x A $\gamma^{-1/2}$ $D^{1/2}$ for the bare CPE to give 0.188cm^2 and 0.063cm^2 respectively.
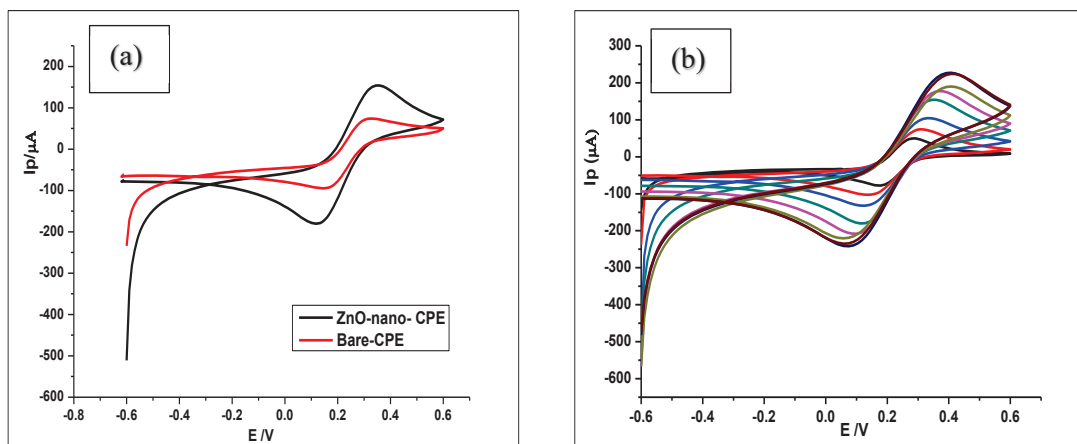.

Figure 3. (a) Voltammograms of Nano-ZnO-CPE and bare CPE (b) Voltammograms of 1 x 10^{-3} mol L^{-1} of $K_3Fe(CN)_6^{3-/4-}$ at different scan rates used for the calculation of the reactive surface area of the modified CPE.

The Nyquist plots of the EIS as can be seen in Figure 4 shows a semi-circular portion which demonstrates an electron transfer limited process, while the linear portion corresponds to a diffusion limited process. The Nyquist diagram shows the electron transfer resistance (R_{ct}) of the both electrodes (bare CPE and Nano-ZnO-CPE), at the bare CPE has a larger R_{ct} and the Nano-ZnO-CPE shows a smaller semicircle, implying a significant acceleration of $Fe(CN)_6^{3-}$ / $Fe(CN)_6^{4-}$, which is evidenced in Figure 3a.
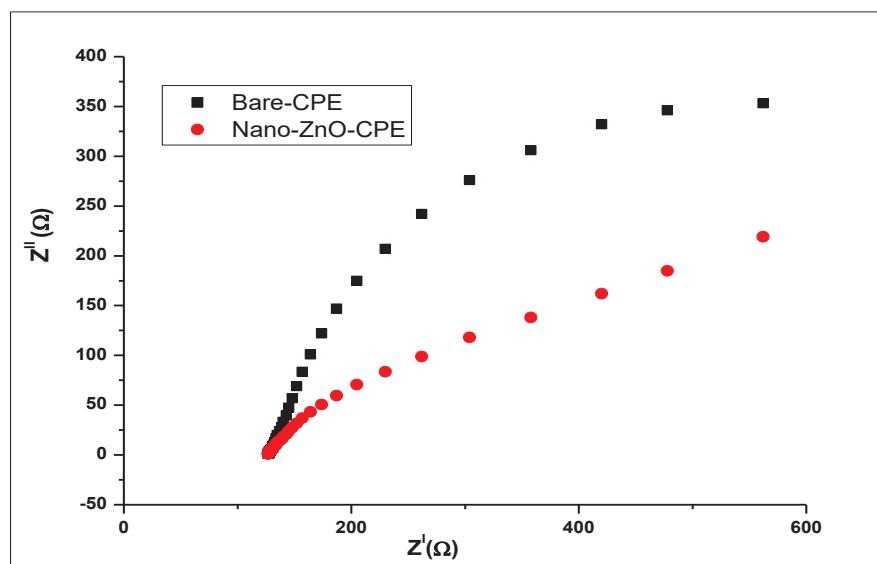

Figure 4. Electrochemical impedance spectroscopy (EIS) at CPE showing the bare CPE and the Nano-ZnO-CPE in a 5mmol L^{-1} $K_3Fe(CN)_6$ – $K_4Fe(CN)_6$. Frequency range from 0.01-100kHz.

Optimization of the electrochemical condition for GA determination was carried out by studying the effect of pH of buffer, effect of scan rate and the effect of the concentration of the analyte. CV scans done on 1 x 10^{-3} mol L^{-1} GA in a pH range of 2 to 8 in 1 x 10^{-1} mol L^{-1} PBS can be seen in Figure 5. From the Figure, the peak current of GA peaked at pH 2 and decreased as the pH increases. Ultimately, the pH of 2 was chosen as the optimal pH condition for the oxidation of GA. In addition, the linear relationship between the peak current and pH shows an equal proton and equal electron took part in the oxidation of GA.
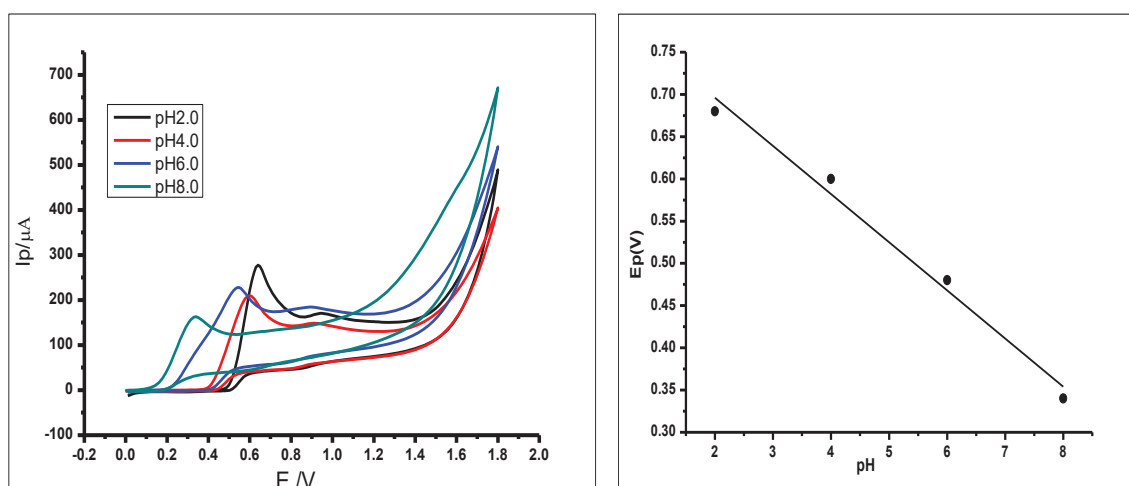

Figure 5a. Cyclic Voltammograms showing the effect of pH on the electrochemical behaviour of 1 x 10^{-4} mol L^{-1} Gallic Acid. (b). Plot of the Peak Potential (Ep) against different pH values, showing the effect of pH on the electrochemical behaviour of 1 x 10^{-4} mol L^{-1} Gallic acid using a ZnO-nanoparticles-CPE at a scan rate of 100mVs^{-1}

The effect of scan rate studied using CV to measure a 1 x 10^{-2} mol L^{-1} GA in 1 x 10^{-1} mol L^{-1} PBS (pH 2.0) showed (Figure 6) increasing peak currents as the scan rates increased from 25 – 1100mV s^{-1}. The linear relationship between the square root of the scan rate and the peak currents (Ip) in the range of 25-1100mV s^{-1} (Figure 6c), produced a linear regression equation described as Ip = -27.408 + 30.809 $\gamma^{1/2}$ (R=0.9944), validating the oxidation of GA in this case as a diffusion-controlled process. On the other hand, looking at the Figure 6a, one can observe a positive shift of the peak potentials as the scan rates increased. Thus, the logarithm of the scan rates vs the anodic peak potential (Ep) has a proportional relationship.
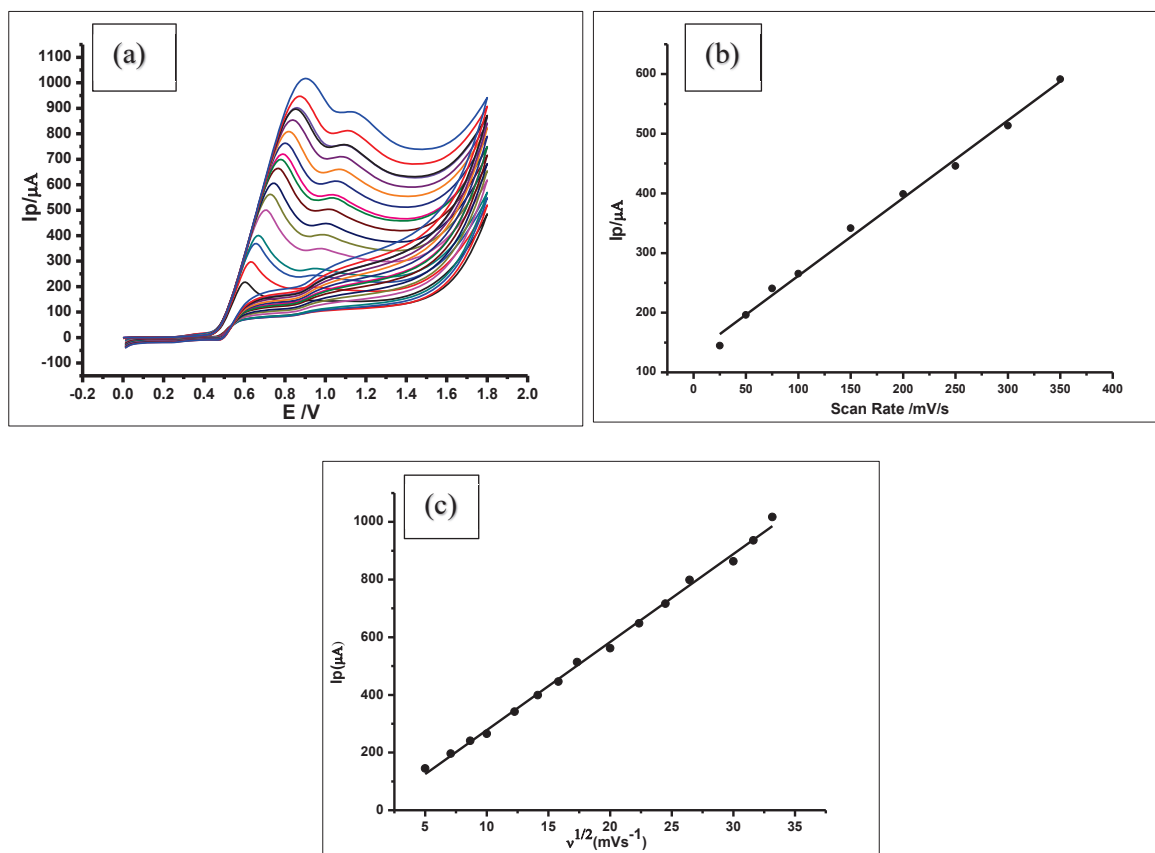
Figure 6. (a) CVs of nano-ZnO-CPE in a 1 x 10^{-1} mol L^{-1} PBS (pH 2.0) with a 1 x 10^{-2} mol L^{-1} GA at a scan rate of 25 to 1100mV s^{-1} (b) the linear relationship between the Ip and the scan rate and (c) the linear relationship between the square root of the scan rate vs Ip.

The determination of GA with different concentrations at the optimized condition was studied using differential pulse voltammetry (DPV), as a more sensitive technique, on the nano-ZnO-CPE in a 1 x 10^{-1} mol L^{-1} PBS (pH 2.0) at a scan rate of 100mV s^{-1} (Figure 7). There was a linear relationship between the increasing concentration of GA and the peak current (Ip). From this concentration range measurements, calibration curves with a linear regression equation of Ip = 2708.7 C (mmol L^{-1}) + 5.3404 with R=0.9968; that produced an LOD of 1.86 x 10^{-7} mol L^{-1}.
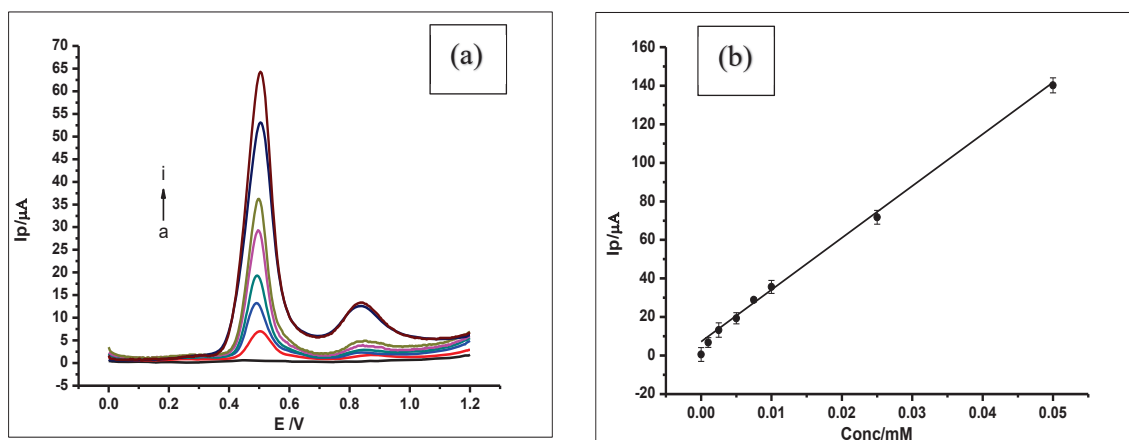
Figure 7a. Differential pulse voltammograms of various concentration of GA at nano-GO-SiO2-nanoparticles in a 0.1 mol L^{-1} phosphate buffer at pH 2.0 at a scan rate of 100mV s^{-1} with voltammograms (a-i) that corresponds to the following concentrations a) 0.0, b) 0.001 mmol L^{-1}, c) 0.0025 mmol L^{-1}, d) 0.005 mmol L^{-1}, e) 0.0075 mmol L^{-1}, f) 0.01 mmol L^{-1}, g) 0.025 mmol L^{-1}, h) 0.05 mmol L^{-1}, i) 0.5 mmol L^{-1}. (Figure 7b) The calibration curve for the determination of GA.

The reproducibility, repeatability and stability of the method using the developed nano-ZnO-CPE was studied. For the reproducibility of the method, the oxidation peaks produced by 8 replicates of 1 x 10^{-3} mol L^{-1} GA measured produced a relative standard deviation (RSD) of 4.9% which is relatively good. Meanwhile for the repeatability of the method, 8 repetitive determination of 1 x 10-3mol L^{-1} GA produced an RSD of 3.63% showing very good repeatability of the method. Finally, the stability was studied, using the same electrode a month apart and got an RSD of 4.25%, depicting a relatively good stability.

The interferences of various species in the determination of 5 x 10^{-3} mol L^{-1} GA, that was investigated by adding different foreign ions (K$^+$, Ca^{2+}, Fe^{3+}, and Na$^+$ then ascorbic acid, caffeic acid and caffeine. The tolerable limits for interference would be the highest amount of the ions that would cause an error of more than 5% in the determination of GA. Looking at Table 1, with RSD values of less than 5% these ions did not interfere with GA.

Table 6. Effects of various substances on the determination of 1 x10^{-3} mol L^{-1} Gallic acid

Interfering Species	Amount in Solution/mol L^{-1}	RSD
Ca^{2+}	1 x 10^{-1}	±2.08
Na+	1 x 10^{-1}	±2.16
Fe^{3+}	1 x 10^{-1}	±1.43
Cl$^-$	1 x 10^{-1}	±2.08
CO$_3^{2-}$	1 x 10^{-1}	±2.16
Ascorbic acid	5 x 10^{-3}	±4.92
Caffeic acid	5 x 10^{-3}	±3.8
Caffeine	5 x 10^{-3}	±3.68

The analytical method (DPV) and the nano-ZnO-CPE was used for the for the determination of GA in red wine; assessing the capability of the modified electrode towards the determination of GA, which was successful with 103% recovery.

4. Conclusion

In this work ZnO nanoparticles were synthesised and characterised, then used for the modification of carbon paste electrode. The ZnO nanoparticles-modified carbon paste electrode were used for the determination of Gallic acid and they showed very good electrochemical capability by enhancing the peak currents produced by the oxidation of Gallic acid. The modified electrode was also successfully used for the detection of GA in red wine.

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