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Determination of Caffeic Acid in Wine Samples Based on the Electrochemical Reduction of Graphene Oxide Modified Screen Printed Carbon Electrode

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An electrochemically reduced graphene oxide was produced by cyclic voltammetric technique and ERGO modified electrode used a new sensor for determination of caffeic acid (CA). The reduced graphene oxide were characterized by Fourier transform infrared spectroscopy (FTIR), Scanning electron microscope (SEM), Raman spectra and cyclic voltammetry (CV). The results reveals electrochemically reduced graphene oxygen content could be decreased significantly. The electrochemical sensor properties examined by cyclic voltammetry and differential pulse voltammetry (DPV). Our proposed sensor ERGO/SPCE exhibited tremendous electrochemically activity towards oxidation of the CA and enhanced current response compared with bare SPCE and GO/SPCE. The wide linear range from 0.2 to 2100 µM and limit of detection 0.064 µM were obtained. The proposed sensor ERGO/SPCE was successfully applied to detection of caffeic acid in wine samples.

Keywords: Caffeic acid; graphene oxide; Electrochemical reduction; screen printed carbon electrode; Wine samples.

1. INTRODUCTION

Graphene, a honeycomb two dimensional lattice structure which consists of single layer sp^2 bonded carbon. Since 2004, the discovery of graphene has received tremendous attention from scientific research around the world due to its unique properties [1-4] such as high surface area, excellent conductivity, and mechanical strength [5-6]. Graphene based composites has been investigated in various application including batteries [7-9], biosensors [10], sensors [11], capacitors [12-], electrocatalysis [13], nanoelectronics [14] and so on.

Generally several methods have been developed to the synthesis of graphene oxide nanosheet such as micromechanical cleavage [15] chemical vapour deposition [16], epitaxial growth [17], and thermal exfoliation [18], Chemical exfoliation of graphite [19].The chemical method most suitable technique to conversion of graphite oxide to graphene because of its low cost and massive product. Although toxic chemical used as reducing agent such as hydrazine, dimethylhyrazine, hydroquinone and metal hydride are hazardous to environment and can break the graphene nanosheets. Recently electrochemical reduction of graphene oxide to produce graphene by using cyclic voltammetry has received great attention because of in this method performed without dangerous chemicals [20]. Interestingly various aqueous and organic [21] mediums NaCl [22], Na_3PO_4 [23], Na_2SO_4 [24], $NaNO_3$ [25], PBS (K_2HPO_4/KH_2PO_4) [26], KNO_3 [27] and KCl [28] have been investigated by electrochemical reduction of graphene oxide to graphene. An external power source (applied potential) is used to drive the reduction process in electrochemical approach and applying more negative potential reduce the oxygen functional group present in the graphene oxide surface [29-32]. Moreover, electrochemically reduced graphene oxide was high conducting and less O/C ratio compared to the chemical methods [33].

Caffeic acid (3-hydroxycinnamic acid) is a kind of phenolic compound are naturally present in plant food, vegetables, cereal and plant derived beverages such as juice, wine and beer [34]. Caffeic acid has been found to be its potential pharmacological application as an antioxidant, antimutagenic, anticarcinogenic agent, lipoxygenase inhibitor, and it also has antimicrobial, anti-inflammatory, and styptic activities [35-37]. Wine contains many phenolic compound, one of them hydroxycinnamic acid also affect the color stability and protection against oxidation, bitterness and clarity [38, 39]. At present, several methods have been developed for determination of caffeic acid in food samples including liquid chromatography and capillary electrophoresis [40]. All these methods have some drawbacks such as high cost and difficult to handle instruments, so on. It should be highlighted that, recently electrochemical technique received considerable attention, because of the easy to handle, more sensitive, good selectivity, and low cost. However, in the literature just a few studies reported which electrochemical technique are used for quantative analysis of caffeic acid in wine samples [41] and mechanism of caffeic acid oxidation [42, 43]. In addition, these methods showed advantages as the determination of caffeic acid at low levels, high sensitivity and selectivity, and a rapid response time.

Our ultimate aim of this work effectively detection of caffeic acid based on electrochemically reduced graphene oxide on the screen printed carbon electrode by electrochemical methods. The as-prepared sensor ERGO/SPCE had excellent analytical performances for determination of Caffeic acid in wine samples. The sensor shows good sensitivity and limit of detection. A simple electrochemical technique were used to construct an electrochemical the sensor and feasible to practical application.

2. EXPERIMENT

2.1. Chemicals

Graphite obtained from Sigma–Aldrich. Caffeic acid was purchased from Aldrich. Screen printed carbon electrode was obtained from Zensor R&D Co., LTD, Taiwan. The supporting electrolyte 0.1 M solution $NaNO_3$ was prepared by using $NaNO_3$ in doubly distilled water. The supporting electrolyte 0.05 M pH 7 solution (PBS) was prepared by using 0.05 M Na_2HPO_4 and NaH_2PO_4 solutions in doubly distilled water. All the other chemicals used in this work were of analytical grade and all the solutions were prepared using doubly distilled water without any further purification.

2.2. Apparatus

Cyclic voltammetry (CV), differential pulse voltammetry (DPV) measurements were performed by using the CHI 900 electrochemical work stations. The surface morphology of as prepared ERGO/SPCE was inspected by using Hitachi S-3000 H Scanning electron microscopy (SEM). Fourier transform infrared spectroscopy (FTIR) was carried out using the JASCO FT/IR -6600 instrument. Conventional three-electrode system was used for the electrochemical experiments; the modified SPCE was used as a working, a saturated Ag/AgCl as a reference electrode and a platinum electrode as the auxiliary electrode. All the electrochemical experiments were performed in an innet atmosphere by purging of N_2 gas into the 0.05M PBS solution.

2.3. Preparation of Reduced graphene oxide modified electrode.

Graphene oxide derived from graphite by the modified Hummer's method as reported previously. The 10 mg of GO was dispersed in 2 ml of deionized water and ultrasonicated for 30 minutes. The 6 µL of well dispersed solution of GO suspension was drop casted on the SPCE and dried at room temperature. The GO modified SPCE was subjected to the electrochemical reduction in 0.1 M $NaNO_3$ at a scan rate of 100 mV/s with potential ranging from 0.0 to -1.5 (5 cycles). The oxygen functional groups content were significantly reduced on graphene oxide at a more negative potential (44). These electrochemically reduced GO modified SPCE was gently washed with deionized water and dried in room temperature. These ERGO modified SPCEs were further used for the physical and electrochemical characterizations. All the electrochemical experiments were performed in ambient conditions and stored in PBS at room temperature when not in use.

3. RESULT AND DISCUSSION

3.1 Characterization

The SEM micrographs of GO and RGO thin films are shown in Figure1 (A&B). The SEM image of GO and ERGO exhibited the surface morphology of graphite platelets changes before and after reduction. It clearly seen in Figure.1A the GO thin curtain like structure with graphite sheets were separated from another sheets after oxidation. This is indication that functionality groups attached to graphene sheets to produced GO [45]. ERGO had a crumpled and wrinkled paper like structure with irregular shape seen in Figure.1B These parameters revealed that graphene sheets well connected together to produced reduced graphene oxide may be due to the functionality group attached to graphene sheets has decreased. These result confirmed that the well aggregated larger surface area reduced graphene oxide successfully prepared using electrochemical techniques.

Fourier transform infrared (FT-IR) spectroscopy provides evidence to the degree of the GO reduction. Figure.1C Shows the FT-IR spectra of the GO and ERGO. The spectrum of the GO showed the presence of epoxy or alkoxy group (C-O) at 1065 cm^{-1}, epoxy symmetrical ring deformation vibration (C-O-C) at 1225 cm^{-1}, Carboxyl (C-OH) at 1400 cm^{-1}, carbonyl (C=C) at 1620 cm^{-1}, and (C=O) in carboxylic acid and carbonyl moieties at 1740 cm^{-1}. At the same time the characteristic absorption peaks of GO nearly disappeared in the FT-IR spectrum of ERGO. Which results confirmed that the effectiveness of the reduction process by using the electrochemical approaches.

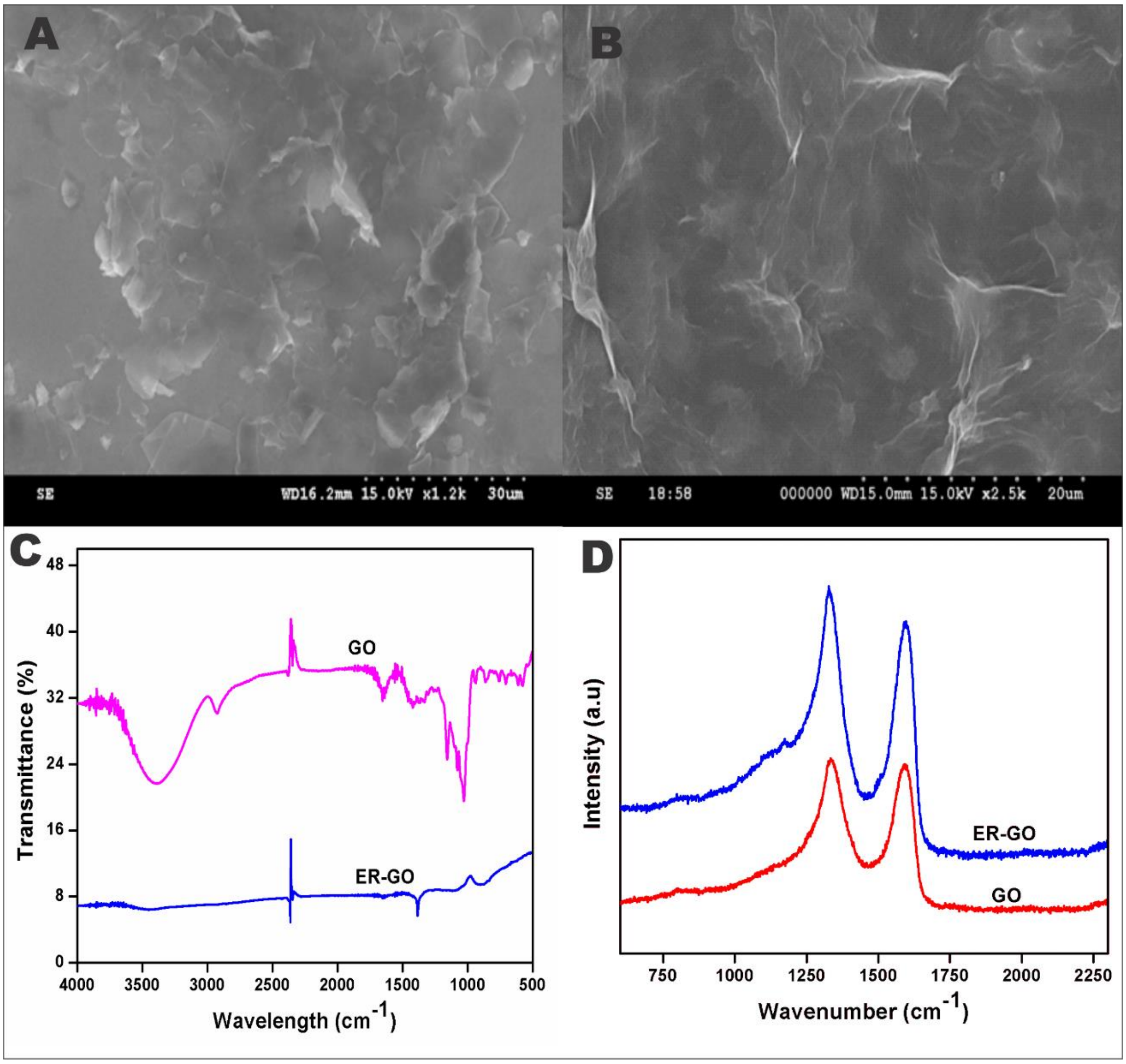

Figure 1. SEM of **A)** GO and **B)** ERGO. **C)** FTIR spectra obtained for GO and ERGO. **D)** Raman spectra obtained for GO and ERGO.

Raman spectroscopy is usually used to characterize the carbon based material structural information. As shown in Figure.1D. The Raman spectrum of GO and ERGO consist of two prominent peaks appeared at 1330 and 1590 cm^{-1}. The two peaks corresponding to well documented D (breathing mode of A1g symmetry) and G (E_2g symmetry of sp^2 carbon atoms) bands, respectively [46]. The structural defects and disorders were measured by calculate intensity ratio of the D and G (I_D/I_G) band [47]. ERGO spectra D band intensity increased indicates forming more sp^2 Domaine. The intensity ratio of ERGO increase significantly compared with that GO. This result suggest that the increased structural defects and disorders during electrochemical reduction process. Summarizing of these results from SEM, FT-IR and Raman spectroscopy confirmed that the successfully formation of the ERGO.

3.2 Electrochemical behavior of CA at ERGO/SPCE

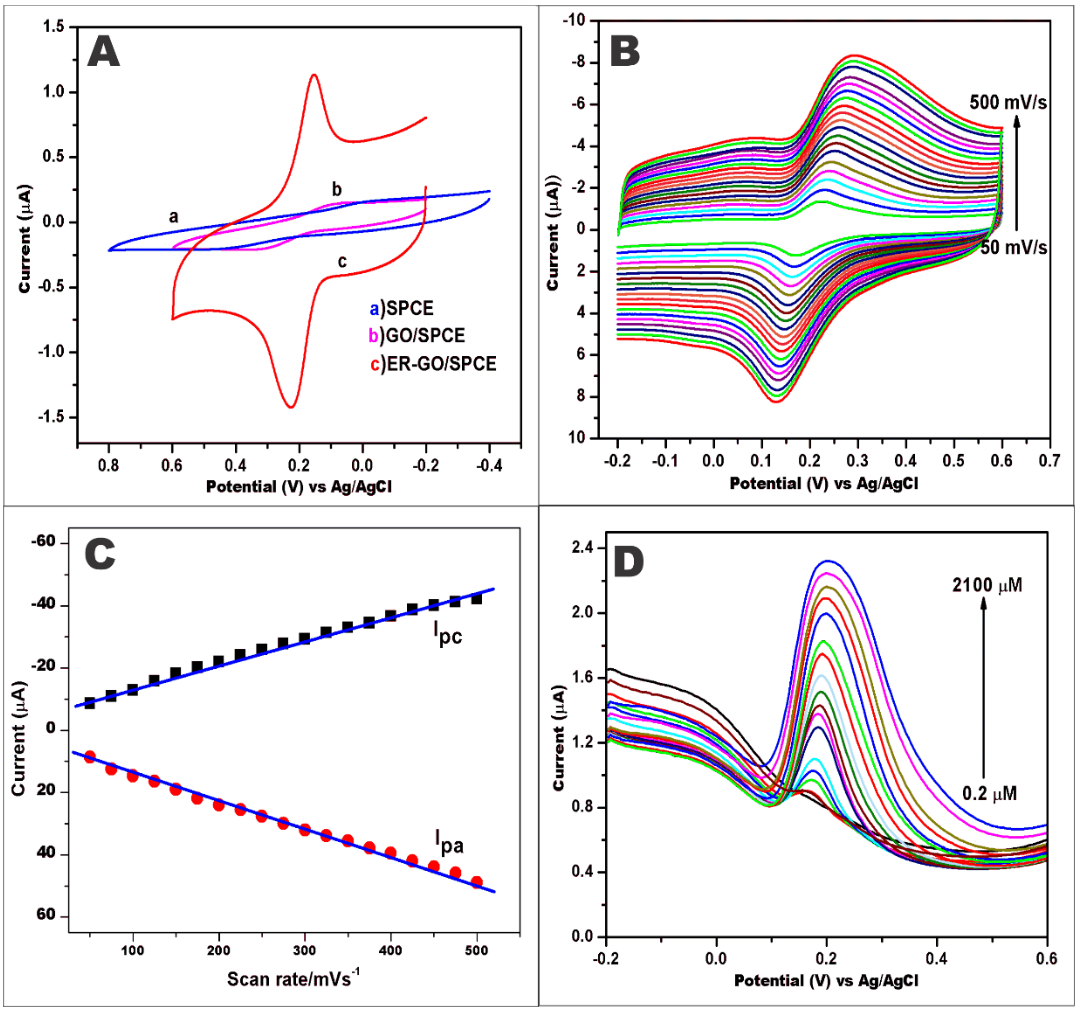

Figure 2. A) CV response of bare SPCE (a), GO/SPCE (b), and ERGO/SPCE (c) in buffer solution pH 7 containing 50 µM CA at scan rate 50mVs^{-1}. **B)** CVs of ERGO/SPCE in buffer solution pH 7 containing 50 µM CA at different scan rate from 50 to 500 mVs^{-1}. **C)** The linear relationship between redox peak current vs scan rates plot. **D)** DPV response for different concentration of CA (0.2-2100 µM) in buffer solution pH.7.

Electrochemical behavior of CA were studied by cyclic voltammetry in pH 7 buffer solution containing 50 µM CA at scan rate 50 mVs^{-1}. Figure.2A shows that the obtained CV response of a)

Bare SPCE b) GO/SPCE and c) ERGO/SPCE towards CA. The result shows that the bare SPCE (a) was exhibited as a weak redox peak at high potential. Moreover, GO/SPCE (b) shows the weak couple of redox peak at 0.325 and 0.0708 mVs^{-1} for CA, peak separation between oxidation/reduction peaks was found to be 0.255 V. Besides, well defined strong pair of redox peak appeared sharply at 0.224 mV negative shift and positive shift at 0.152 mV, with peak distance Ep of 0.072 mV for ERGO/SPCE (c) towards oxidation of CA. ERGO/SPCE performance exhibited an enhanced current was 10 time higher than that of the GO/SPCE and Bare SPCE, with a peak to peak distance value is very smaller than GO/SPCE. The enhanced electrical conductivity of the ERGO/SPCE is due to the electrochemical reduction process remove the oxygen content on the surface of the GO became a rougher surface and high expose electrochemical active sites and its provides optimistic sites for the transmit of electrons to CA. The ERGO/SPCE exhibited effective electrochemical properties towards CA than GO/ SPCE. This result confirmed that the ERGO modified SPCE greatly accelerate the electron transfer rate to reversible oxidation CA.

3.3 Effect of scan rate

The effect of scan rate dependence of the redox peak current of CA for ERGO/SPCE evaluated result depicted in Figure.2B. It can be seen that the couple of redox peak current of CA linearly increased with the scan rate increases. The anodic and cathodic peak current response gradually increased proportional to the scan rate from 50 mV to 500 mV. Hence, the scan rate increased, linearly the oxidation peak shift to more positive potential and the reduction peak shift to more negative side. Figure.2C shows that the oxidation CA current value plotted against scan rates. The linear regression equation for the oxidation peak was I_{pa} (µA) 0.0816x + 6.7153 with Correlation coefficient R^2 =0.9926 and for the counterpart peak current was I_{pc} (µA) -0.0753x +6.3152 and Correlation coefficient R^2 =0.9935. This result indicated electron transfer rate was slow on the surface of ERGO modified electrode. These result confirmed that the ERGO/SPCE effective catalytic active towards CA overall oxidation reduction process controlled by adsorption phenomenon.

3.4 Determination of caffeic acid

Our ultimate aim this study was to introduce the uncomplicated and economical method for determination of caffeic acid. DPV response for CA oxidation at ERGO/SPCE were examined. Figure.2D shows the different concentration of CA at ERGO/SPCE were studied by DPV. It can be seen that the well-defined peak current increased with increasing concentration of CA in the range from 0.2 to 2100 µM. The calibration curve expressed two linear segments (Figure.3). The first linear segment from 0.2 to 100.75µM with a correlation coefficient R^2 = 0.9929 and the second linear observed from up to 2100 µM with a correlation coefficient R^2 = 9910. The linear ranges reflect the adsorption process of CA at ERCO/SPCE surface. The limit of detection was calculated 0.064 µM at s signal to noise ration 3 (S/N) and sensitivity of for first segment 0.6564 (µA µM^{-1} cm^{-2}) and second segment value 0.0352 (µA µM^{-1} cm^{-2}) obtained. This lower detection limit and wide linear range concentration of CA were compared to previous reported methods [48-54] summarized in Table 1.

Ezhil Vilian et al. have reported determination of CA by CRGO modified GCE [55] it necessary long time groundwork and they using complex procedure and Hayati Filik et al also have reported the determination of CA by using Nafion/ER-GO/GCE [56] it also requiring long time preparation and high cost chemicals, it can be making these electrodes as expensive. However, the reported procedure is very simple, less time taken, easy to handle. Compared to earlier reported CA sensors, our ERCO/SPCE having oxidation potential of CA is much lower and lesser LOD was achieved than the other reported sensors. These result indicated that the proposed sensor ERGO/SPCE was a better advantageous to determination of CA than other methods.

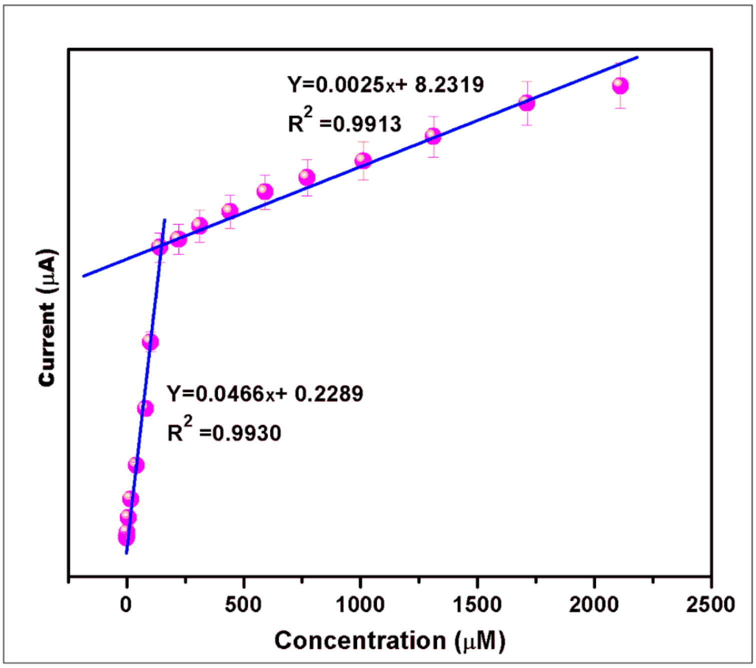

Figure 3. The linear relationship obtained between the DPV responses of various concentration of CA with corresponding peak currents.

Table 1. Comparison of the analytical performance of CA with previous reported methods.

Modified Electrode	Method	Linear range (µM)	Limit of detection (µM)	Ref.
Laccase biosensor (LTV-SPE)[a]	Amperometric	0.5–130	0.524	[48]
Laccase-MWCNT-chitosan/Au[b]	Amperometric	0.735–10.5	0.151	[49]
Poly(Glutamic Acid)/GCE	SWV	4–30	3.91	[50]
Activated GCE	DPV	0.1–1	0.068	[51]
ERGO/Nafion	SW-AdSV	0.1 – 10	0.09	[52]
EPD-LuPc/ITO	CV	60-500	3.12	[53]
Glassy polymeric carbon	DPV	0.1-96.5	0.29	[54]
ERGO/SPCE	DPV	0.2-2100	0.064	This work

[a] laccase (Trametes versicolor), screen-printed electrode; [b] gold sheets electrode

3.5 Interference studies

The influence of some foreign compounds potentially interfering with the determination of caffeic acid was studied under optimized electrochemical conditions. Caffeic acid will be generally suffered with some analogous structure compound were potential interferants such as ascorbic acid, ferulic acid, gallic acid, coumaric acid and uric acid. The effect of ascorbic acid, ferulic acid, gallic acid, coumaric acid and uric acid on the detection of CA were studied. It was found that the 100 fold excess of interferants ions did not interfere for oxidation of CA at ERGO/SPCE. These result confirmed that the proposed sensor had a high selectivity towards determination of CA with interferants.

3.6 Stability, Repeatability and Reproducibility

The estimation of reproducibility of sensor studied by DPV. Five GO/SPCE were electrochemically reduced based on the similar condition and their individual current and potential response of 30 µm CA was recorded in pH 7 at PBS buffer solution. The relative standard deviation (RSD) was calculated to be 2.8 % was obtained, these results indicating that the considerable reproducibility. In addition, the repeatability of ERGO/SPCE is also examined by 10 successive determination of 30 µm CA, the calculated RSD was 3.2 % proving that the ERGO/SPCE had good repeatability of sensor. Besides, storage stability of the modified electrode was investigated by measuring peek current response after five weeks the sensor where stored in refrigerator for (4°C) when not in use and we got decreased by 4.62 % of its initial peek current response of CA. These results indicated that the proposed sensor had a great reproducibility, repeatability and huge storage stability against the CA determination and does not suffer from storage environment.

3.7 Real samples analysis

Table 2. Determination of CA in wine samples (n=3)

Samples	**Added (µM)**	**Found(µM)**	**Recoveries (%)**
A	5.0	4.98	99.6
	10.0	15.11	102.1
	20.0	34.82	98.6
B	5.0	5.14	102.8
	10.0	14.86	97.2
	20.0	34.64	98.9
C	5.0	4.93	98.6
	10.0	15.02	100.9
	20.0	35.23	101.0

The practicability of the sensor was applied to determination of CA in wine samples under optimized condition using standard addition method. Different wine samples were purchased from local alcohol market. Similar optimized experimental conditions were applied to CA determination in wine samples (A, B and C). The obtained results presented in the Table 2. For each addition of wine samples three measurements were taken. The obtained results are considerable as the recovering rate falls. Considering the concentration of CA samples directly analyzed without need of sample treatment. This results conclude that the ERGO/SPCE has used for practical application for accurate and sensitive detection of CA in wine samples.

4. CONCLUSION

In this study, we have successfully prepared electrochemically reduced graphene oxide film modified screen printed carbon electrode (ERGO/SPCE) and developed as highly selective electrochemical sensor for CA. This sensor was prepared relatively simple with quick time. The ERGO/SPCE exhibits a good performance in terms of sensitivity, lower detection limit, wide linear range, long time stability, reproducibility, repeatability in caffeic acid determination. Moreover, the proposed sensor ERGO/SPCE was applied to determination of CA in wines was also proved with satisfactory results.

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