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Square-wave stripping voltammetric determination of caffeic acid on electrochemically reduced graphene oxide–Nafion composite film

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ABSTRACT

An electrochemical sensor composed of Nafion–graphene nanocomposite film for the voltammetric determination of caffeic acid (CA) was studied. A Nafion graphene oxide-modified glassy carbon electrode was fabricated by a simple drop-casting method and then graphene oxide was electrochemically reduced over the glassy carbon electrode. The electrochemical analysis method was based on the adsorption of caffeic acid on Nafion/ER-GO/GCE and then the oxidation of CA during the stripping step. The resulting electrode showed an excellent electrocatalytical response to the oxidation of caffeic acid (CA). The electrochemistry of caffeic acid on Nafion/ER-GO modified glassy carbon electrodes (GCEs) were studied by cyclic voltammetry and square-wave adsorption stripping voltammetry (SW-AdSV). At optimized test conditions, the calibration curve for CA showed two linear segments: the first linear segment increased from 0.1 to 1.5 and second linear segment increased up to 10 μM. The detection limit was determined as 9.1×10^{-8} mol L^{-1} using SW-AdSV. Finally, the proposed method was successfully used to determine CA in white wine samples.

1. Introduction

Caffeic acid (3,4-dihydroxycinnamic acid) (CA) is a general phenolic acid that are naturally present in many agricultural products, such as, fruits, vegetables, wine, olive oil, and coffee. Phenolic acids are also found in plant foods, mostly in bound form. Wine is considered as a rich source of phenolic acid and flavonoids but the phenolic amount varies considerably in the various wine types, depending on the grape variety, environmental factors in the vineyard and the wine processing techniques. The most common hydroxycinnamic acids are caffeic, *p*-coumaric and ferulic acids, which are frequently found in foods as simple esters besides quinic acid or glucosides. The most well-known bound hydroxycinnamic acid is cholorogenic acid, which is combined from caffeic and quinic acids [1]. Chlorogenic acid, generally present in table wines, decreases with age. Caffeic acid is formed later in the maturation process [2]. Caffeic acid (CA) is a kind of polyphenol that is widely distributed in higher plants as glycosides, esters and the free form. CA esters display selective antiproliferative activity against some types of cancer cell [3]. Wine samples are complex beverages that contain numerous components influencing wines quality attributes. Caffeic acid is one of the phenols present in abundance in red wine and also contributes to color stability and protection against oxidation. Caffeic acid is an antioxidant and it can also act as a carcinogenic inhibitor. Thus, it is imperative to establish a simple, fast, sensitive and low cost method for the quantitative analysis of caffeic acid.

Several techniques, such as, liquid and gas chromatography, capillary electrophoresis and spectrophotometry have widely been applied to the determination of phenolic acids in food samples and plant materials. Electroanalytical techniques, of voltammetric techniques, were particularly well suited to the analysis of polyphenols. Typical electrochemical sensing of polyphenols in wines was carried out using direct electrochemical oxidation over carbon-based or metallic electrodes. The oxidation of caffeic acid (CA) over various electrode materials (platinum, carbon, gold, etc.) in aqueous acid medium was shown to form an electroactive polymer material [i.e., poly(caffeic acid)]. The obtained polymer was characterized, its electrochemical and electrochromic properties were investigated and the polymer material employed to sensors [4–10]. The oxidation of caffeic acid led to the formation of the corresponding *o*-quinone through disproportionation of the initial semiquinone radical. In the case of *p*-coumaric acid and ferulic acid, the initial radicals decayed by a second order kinetics via a radical–radical coupling mechanism [11]. Concerning the

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electrochemical measurements, most of them are focused on the study of the mechanism of caffeic acid oxidation [4–11]. Hotta et al. have investigated the electrochemical oxidation mechanism of CA. They indicated that a semi-quinone radical and quinone may undergo a further dimerization, although the oxidation processes are not fully understood [12]. Very recently, Arakawa et al. used a micro flow electrolytic cell on-line with electrochemistry/electrospray ionization mass spectrometry (EC/ESI-MS) to study the oxidation of the highly antioxidative agent, caffeic acid. Dimer products were detected at electrolytic potentials of $E=0.7$ V (vs. Ag/AgCl) and trimer products at 1.0 V at pH 9 [13].

There were few electrochemical studies aimed for the quantitative determination of caffeic acid in different matrices. Sousa et al. reported the electrochemical oxidation of cinnamic acid derivatives (caffeic and chlorogenic acids) by cyclic voltammetry on glassy carbon electrode and modified glassy electrode [6]. The deposition of the caffeic acid on the electrode surface (i.e. GCE) was carried out by dipping the electrode and by cycling the potential in a solution containing the phenolic compound. They found a selective interaction between activated GCE and CA and this interaction allowed CA's detection and determination in complex matrices, such as, orange juice without the ascorbic acid interference [6]. So far, various modified electrodes have been used for the electrochemical determination of CA, for example, poly(glutamic acid) (PG) film modified GCE [14], glassy polymeric electrode modified with poly(caffeic acid) film [15], lead film modified GCE (PbFE-GCE) [16]. Recently, a biosensor based on green bean (*Phaseolus vulgaris*) tissue homogenate as a source of peroxidase was constructed in order to determine caffeic acid in white wine by using square-wave voltammetry [17]. To the best of our knowledge, there was no report using Nafion/graphene modified electrodes for the determination of CA. Graphene, the 2D honeycomb lattice of sp^2-bonded carbon atoms, has attracted tremendous attention from both theoretical and experimental scientific communities in recent years [18–21].

In this study, we prepared the Nafion/ER-GO composite film modified glassy carbon electrode (GCE) for the electrochemical determination of caffeic acid. The electrochemical quantitation of caffeic acid on the Nafion/ER-GO film was investigated in detail. The square-wave adsorption stripping voltammetric (SW-AdSV) techniques in this study can be used for the sensitive determination of CA in white wine samples. Compared with the bare glassy carbon electrode, ER-GO-modified electrode could extensively enhance the redox peak currents and decrease the overpotentials of CA. The results of this study were compared to those obtained by high performance liquid chromatography (HPLC).

2. Experimental

2.1. Apparatus

Cyclic voltammetry (CV) experiments were carried out with a Gamry Reference 600 potentiostat (Gamry, USA) attached with a platinum wire as the counter electrode, a glassy carbon electrode (3 mm diameter) as working electrode and Ag/AgCl (3.0 M KCl) reference electrode. All experiments were performed at room temperature (25 °C). Prior to each experiment, the working electrode was polished with slurry containing 0.3 μm and then 0.05 μm sized aluminum oxide particles for 5 min. After each treatment, the electrode was washed and ultrasonicated in distilled water for 5 min to remove retained aluminum oxide particles on the electrode surface. The pH values of the solutions were measured by a Hanna HI 221 pH-meter using the full range of 0–14. A Waters Breeze™ 2 Model HPLC system (Milford, MA, USA) equipped with a 1525 binary pump, a column thermostat, a 2998 photo-diode array detector, (Chelmsford, MA, USA), was used for chromatographic measurements. Injections were done using a 25-μL syringe (Hamilton Co., Reno, NV). Scanning electron micrographs (SEMs) were obtained using an FEI - QUANTA FEG 450 SEM. Graphite and graphene oxide crystallographic structures were analyzed using a Rigaku D/max-2200 Ultima X-Ray diffractometer with Cu Kα radiation.

2.2. Reagents and solutions

Acetate buffer solution was prepared by mixing the stock solutions of 0.1 M CH_3-COOH and 0.1 M CH_3-COONa at various ratios to adjust the pH value of 5.0. All other chemicals were of analytical grade. All experiments were carried out in a supporting electrolyte of acetate buffer (0.1 M, pH 5.0) at room temperature (25 ± 1 °C). Cyclic voltammetric experiments were performed with a scan rate of 100 mV s^{-1}. The caffeic acid (CA) was obtained from Fluka (of 99% purity). A stock solution of CA was prepared by a dissolving 0.01 g reagent in 10 mL of ethanol and stored at 4 °C in the dark until used. The working solutions were prepared by appropriate dilution of a stock solution in distilled water. 5.0 wt% Nafion® solution in water–isopropanol was obtained from Solution Technology Inc. (equivalent weight 1100 g/mol sulfonic acid groups). 1.0 wt% Nafion solution was prepared by diluting the 5.0 wt% Nafion solution with isopropyl-alcohol. Graphene oxide (GO) was synthesized from natural graphite by a modified Hummers method [18,22]. The synthesized GO sheets were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Graphene used in this experiment was prepared through electrochemically reduced graphene oxide (GO) [23].

2.3. Determination of caffeic acid

A three-electrode system was used, including a Nafion/ER-GO/GCE as the working electrode, a platinum electrode as a counter electrode, and Ag/AgCl (3.0 M KCl) as a reference electrode. Nafion/ER-GO modified glassy carbon electrode was prepared according to a literature reported procedure [23,24]. The electrodes were dipped in the acetate buffer solutions. After recording the square-wave adsorption stripping voltammogram (SW-AdSV) of the blank solution, an accurate concentration of the CA solution was added and measured. The optimized experimental conditions for the stripping voltammetric determination of CA were: 0.1 acetate buffer solution (pH = 5.0) as supporting electrolyte, step size = 8 mV, frequency (f) = 10 Hz, pulse size = 100 mV, accumulation time = 300 s, and accumulation potential $E = -600$ mV.

3. Results and discussion

3.1. Advantages of ER-GO

In this work, graphene oxide (GO) is electrochemically reduced to produce graphene, which we call electrochemically reduced graphene oxide (ER-GO). The electrochemical reduction removes partial oxygen from GO and also increases the hydrophobicity of graphene sheets. The electrochemical reduction of GO, the ER-GO film shows a more large wrinkle and a rougher surface than the GO film. Such rough surface may facilitate the penetration and diffusion of electrolyte ions. The electrochemical reduction of GO can efficiently expose electrochemically active sites. Briefly ER-GO exhibits higher electrochemical capacitance and cycling durability than GO, chemically reduced graphene and carbon nanotubes [25,26].

3.2. Cyclic voltammetry of caffeic acid

The electrochemical behavior of CA was studied by cyclic voltammetry (CV) in a pH 5.0 acetate buffer solution. It was found that bare GCE showed a weak electrochemical response towards CA (Fig. 1a). The separation between the oxidation/reduction peak potential (ΔE_p) was found to be 248 mV (E_{pa}=0.404 V, E_{pc}=0.156 V). The CV of the Nafion/ER-GO/GCE in pH 5.0 acetate buffer solution without CA only showed a capacitive current (Fig. 1b). When CA (2.0×10^{-4} M) was added into acetate buffer solution, a pair of well-defined redox peak was observed at the Nafion/ER-GO/GCE (Fig. 1c). A pair of sensitive redox peaks for CA with a peak-to-peak separation was found to be ΔE_p=152 mV (E_{pa}=0.404 V, E_{pc}=0.252 V), which is much smaller than that of a bare GCE (ΔE_p=248 mV). Nafion/ER-GO/GCE was found to be a sensitive electrochemical sensor for electrocatalytic determination of CA (Fig. 1c). In addition, the anodic peak current signal of CA at the Nafion/ER-GO/GCE was 17-fold higher than that of a bare GCE. The results of this study indicated that graphene greatly accelerated electron transfer rate, due to its unique physicochemical properties (the sheets like nature, high conductivity, large surface area, etc.) [27].

3.3. Effect of scan rate

The scan rate dependence of the redox peak currents and the peak-to-peak separation was also studied, and the results were depicted in Fig. 2. The peak current of CA increased linearly with the scan rate (ν) increase. This meant that the electrode process was controlled by adsorption. On the other hand, with the increase of the scan rates, the oxidation peaks shifted to more positive potentials, while the counterpart peaks shifted to more negative potentials. Since counterpart peaks shifted with smaller potential in comparison with the larger oxidation potential shifts, this findings indicated that the electron-transfer rate was not very fast and hence, the electrochemical reaction gradually became less reversible. The linear relationship between the peak current and scan rate were expressed by the linear regression equation as: $I_{pa}/(\mu A)=26.07+0.686\ \nu/\text{mV s}^{-1}$ (R=0.9916) and $I_{pc}/(\mu A)=-11.34-0.598\ \nu/\text{mV s}^{-1}$ (R=0.9924), respectively. At scan rates ranging from 25 to 500 mV s^{-1}, the linear regression equations of E_{pa} and E_{pc} as well as the logarithm regression equations vs. the scan rates were expressed as $E_{pa}=0.313+0.0306\log\nu$ (R=0.9910) and $E_{pc}=0.027\ \ 0.0247\log\nu$ (R=0.9951), respectively. According to Laviron theory [28], the slopes are equal to $2.3RT/(1-\alpha)nF$ and $-2.3RT/nF$ for anodic and cathodic peak, respectively. Thus, the electron transfer coefficient (α) and the electron transfer number (n) were calculated to be 0.58 and 2.24, respectively.

3.4. Effect of pH

The effect of solution pH on the redox response of 2.0×10^{-4} M CA was investigated in 0.1 mol L^{-1} acetate buffer solution by cyclic voltammetry. Fig. 3 showed the influence of solution pH on the peak current and peak potential. The cathodic and anodic peak potentials shifted to more negative values. As shown in Fig. 3, the redox peak current signal increased with solution pH ranging from 3.6 to 5.0, and beyond this pH range, the decrease of the redox peak current signal was observed. Considering the determination sensitivity, pH 5.0 was chosen in the following investigation. When the pH exceeded 8.0, the cathodic peak signal disappeared completely. This observation was explained as to the protons taking part in the electrochemical reaction. Thus, a buffer solution of pH 5.0 was selected as the optimal supporting electrolyte for CA sensing in the following experiments. As can be seen in Fig. 3, with increasing pH value of the solution, the redox peak negatively shifted; based on $E_p=(E_{pa}+E_{pc})/2$, the equation was $E_{pa}=0.6375-0.0589$ pH

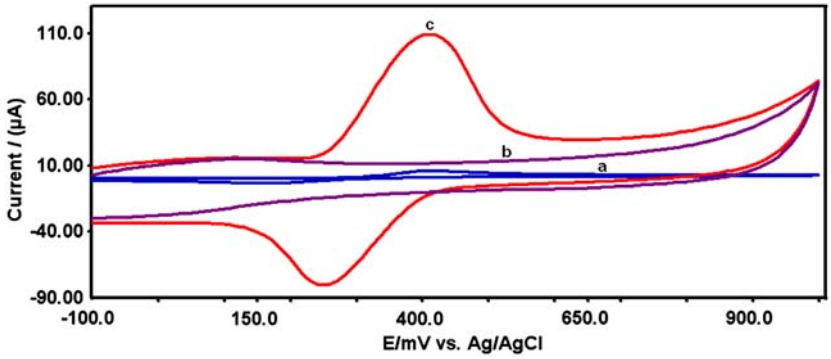

Fig. 1. CVs recorded at a bare GCE (a) with 0.2 mM CA; Nafion/ER-GO/GCE with (c) 0.2 mM CA and without CA (b) in the 0.1 M acetate buffer, pH 5.0, scan rate: 100 mV s^{-1}.

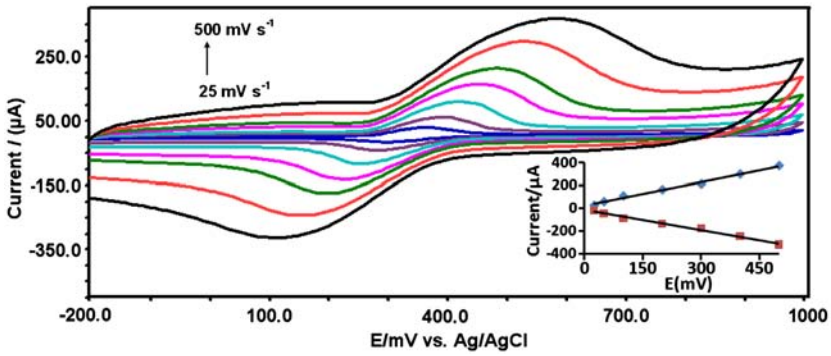

Fig. 2. CVs of 0.2 mM CA at Nafion/ER-GO/GCE with different scan rates from 25 to 500 mV s^{-1} (25, 50, 100, 200, 300, 400, and 500, respectively) in 0.1 M acetate buffer (pH 5.0). Inset: plot of both anodic and cathodic peak currents vs. scan rate.

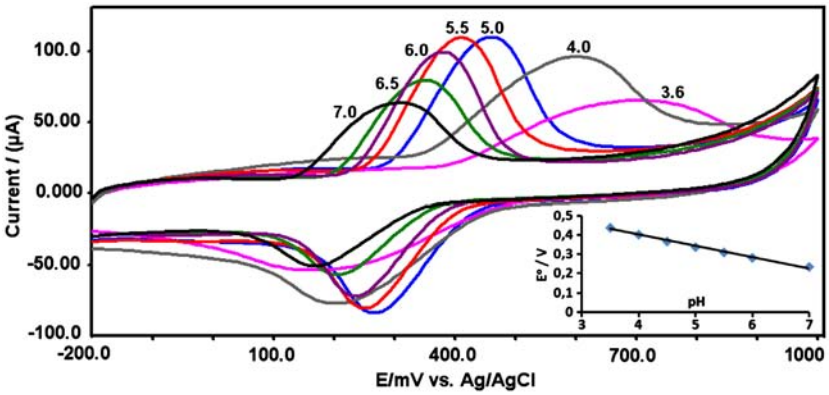

Fig. 3. Cyclic voltammetry responses in different buffered solutions: pH 3.6 to pH 7.0. The inset shows a plot of the formal potential vs. pH.

(r=0.9944), where the peak potential was expressed in V. According to the Nernst equation, the slope of −59 mV pH^{-1} revealed that the proportion of electrons and protons involved in the reactions was found to be 1:1. Since CA oxidation was a two-electron process, the number of protons involved was also found to be two. This finding was in line with findings of a previous report [4–14].

3.5. Effect of potential cycling

The potential cycling for the oxidation of caffeic acid in 0.1 M acetate buffer was carried out over the Nafion/ER-GO composite modified GCE. Cyclic voltammograms of CA were recorded at a scan rate of 100 mV s^{-1}. Successive cyclic voltammograms of CA were then recorded. At the first cycle, higher peak intensity was observed at ~0.40 V potential. After the first cycle, the Nafion/ER-GO modified electrode was rinsed with distilled water and transferred into a supporting electrolyte acetate buffer (pH 5.0) solution, where cyclic voltammograms were again recorded. The peak current of CA was still observed, however, it decreased gradually. The values of the peak current obtained after several repetitions (40 cycles) were almost unchanged. This behavior indicated that the use of a Nafion/ER-GO modified electrode strongly retained the poly(caffeic acid) on the electrode surface at pH 5.0, which was removed only by scrubbing with alumina powder.

3.6. SW-AdSV parameters

The peak currents depend on the SW-Ad stripping voltammetric parameters. To achieve the maximum sensitivity of SW-AdS peak, step size, pulse size, frequency (f), accumulation potential and time parameters have to be carefully optimized. The oxidation peak currents were then obtained under different pHs, pulse sizes, frequencies, accumulation potentials, and times. The highest response of the current was obtained at pH 5.0 similar to those found in cyclic voltammetric experiments. Stripping peak currents were increased with pulse sizes up to 100 mV, but the base-line current also increased. The stripping peak intensity initially increased with frequency from 5 to 50 Hz, and then became distorted and ill-defined. The stripping peak current increased linearly with the step size up to 8 mV. Accumulation by the adsorption of CA (1.0×10^{-6} mol L^{-1}) on the electrode surface, could enhance the current response and improve the detection sensitivity. Therefore, the effect of accumulation time and accumulation potential was investigated by SW-AdSV. The accumulation potentials from −0.2 V to −1.0 V were applied under stirring at 400 rpm. The stirring was stopped, and after waiting for 5 s equilibrium period, the stripping voltammogram of CA was recorded. The results indicated that the highest efficiency of the accumulation of CA was obtained when the accumulation potential was equal to −0.60 V, so for further studies this potential was utilized. When the accumulation potential was more negative than −0.6 V, the stripping peak current changed only very slightly while the background current increased greatly. The effect of the accumulation time was studied for a CA concentration of 1.0×10^{-6} mol L^{-1}. The accumulation time was tested in the range from 60 to 360 s. The peak current of CA increased significantly with the increase of the accumulation time, and reached a maximum at 300 s, suggesting that Nafion/ER-GO/GCE can rapidly accumulate CA. Then, the current increased slightly when the time exceeded 300 s. Therefore, 300 s was used as the accumulation time.

3.7. Interferences

The determination selectivity is an important property for any analytical technique. It was well known that caffeic acid generally suffered from the interferences of ascorbic acid as well as coumaric, sinapic and ferulic acid (i.e. Cinnamic acid derivatives). Hence, a systematic study of interferences due to ascorbic acid, coumaric, sinapic, ferulic acid and gallic acid was carried out. The result showed that 100-fold of coumaric, sinapic, ferulic, gallic and ascorbic acid did not interfere with the SW-AdSV signal for the oxidation of CA (1.0 μM) on the Nafion/ER-GO/GCE, indicating that the modified electrode was highly selective towards caffeic acid quantitative determination (peak current change $<5\%$). However, a major problem was that the oxidation potentials for caffeic acid (CA) and chlorogenic acid (CGA) occurred almost in the same potential at modified electrodes, which resulted in overlapped voltammetric responses, making their discrimination highly difficult. As an example, comparison of the response of chlorogenic acid at the Nafion/ER-GO film-modified electrode was provided. The redox peak current of chlorogenic acid at the fabricated electrode was lower than the redox peak current of caffeic acid. The ratios of the concentration of caffeic acid to that of each substance were fixed at 1:1. Chlorogenic acid caused a positive interference (14.0%) when present at the same concentration as the analyte. This positive interference observed was not critical, because chlorogenic acid was present at lower concentration levels than those investigated (i.e., white wine samples) [3]. The effect of catechin on the stripping voltammetric determination of 1.0×10^{-6} mol L^{-1} caffeic acid was also studied. On the basis of the obtained results it could be stated that the determination of CA was not influenced by a 20-fold excess of catechin.

3.8. Reproducibility and stability

To estimate the fabrication reproducibility of the Nafion/ER-GO modified electrode, the relative standard deviations (RSD) of five electrodes prepared independently for measuring 1.0 μM CA was

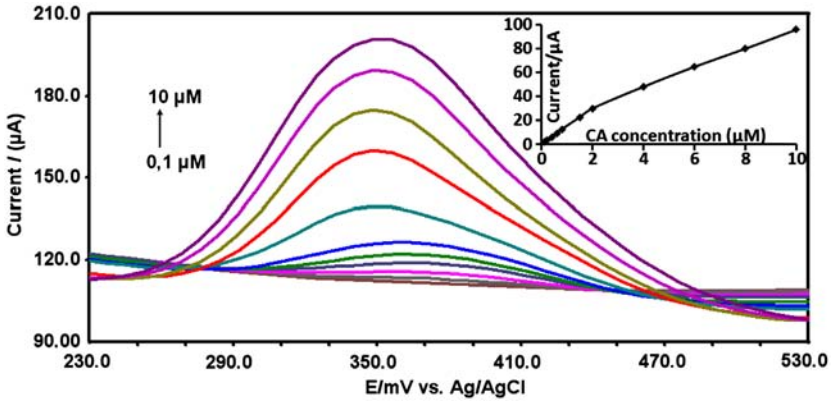

Fig. 4. SW-AdVs of 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 4.0, 6.0, 8.0, and 10 μM of CA at Nafion/ER-GO/GCE in 0.1 M acetate buffer (pH 5.0). Caffeic acid was accumulated for 300 s at −0.60 V. Inset, the plot of peak current vs. CA concentration.

calculated to be 3.28%, proving the good fabrication reproducibility. The measurement repeatability of the Nafion/ER-GO modified electrode was tested with the same CA concentration. The RSDs of 1.0 and 5 μM CA were 3.7% and 3.5% for 10 repetitive assays, respectively. This result alone indicated that this method had good reproducibility. The response of the Nafion/ER-GO modified electrode to 1.0 μM CA only decreased 4.64% of its initial response after stored in refrigerator at 4 °C for 20 days.

3.9. Analytical parameters

The voltammetric determination of CA was carried out in 0.1 M acetate buffer (pH 5.0) using square-wave adsorptive stripping voltammetry (SW-AdSV) at the Nafion/ER-GO/GCE. Fig. 4 showed the square-wave adsorptive stripping voltammograms (SW-AdVs) of various concentrations of CA. The peak currents increased linearly against the concentration of CA within the range of 0.1–10 μM. The calibration curve for CA showed two linear segments: the first linear segment increases from 0.1 to 1.5 μM with an regression equation of $I_p/(\mu A)=0.4449+14.731\ C/\mu M$ ($R=0.9992$), and the second linear segment increases up to 10 μM with an regression equation of $I_p/(\mu A)=13.894+8.2586\ C\ (\mu M)$ ($R=0.9990$). At higher concentrations than 10 μM, a clear deviation was observed. The two linear ranges of CA most likely reflected the formation of a CA monolayer in the first range of calibration and the multilayer adsorption of CA in the second range during the accumulation process where CA was preconcentrated onto the Nafion/ER-GO/GCE. The limit of detection of CA was 0.091 μM (9.1×10^{-8} mol L^{-1}) and calculated by using the equation for (LOD)=3 s/S [29]. The limit of detection of CA at the Nafion/ER-GO/GCE was substantially lower than those obtained on glassy carbon electrode and modified glassy carbon electrode (*ie.*, quinones, imidazolic groups and enzymes electrodeposited) (LOD = 1.0×10^{-5} mol L^{-1}) [12], poly(glutamic acid) modified glassy carbon electrode (LOD = 1.25×10^{-6} M) [13], glassy polymeric carbon electrode (LOD = 2.9×10^{-7} M) [14], and green bean tissue homogenate-based biosensor (LOD = 2.0×10^{-6} mol L^{-1}) [16], The present method based on Nafion/ER-GO/GCE had a much higher sensitivity compared with the above-mentioned electrochemical methods [12–14,16]. These results indicated that Nafion/ER-GO/GCE was an appropriate and advantageous platform for the determination of caffeic acid.

3.10. Analytical applicability

The applicability of the voltammetric procedure was confirmed by the determination of CA acid in white wine samples obtained from the markets of Istanbul/Turkey. The accumulation was performed without any previous preparation, but just through adequate dilution of the sample in acetate buffer pH 5.0. The quantification of the caffeic acid in white wines was also accomplished by the standard addition method. Typical square-wave adsorptive stripping voltammograms of caffeic acid oxidation were obtained, and the peak current increased with standard addition of caffeic acid. The recoveries were in the range from 97% to 98%. The determination of CA was performed and the results were shown in Table 1. The experimentally obtained values were in line with values reported in the literature which were in the 0–6 mg L^{-1} for commercial white wines samples, respectively [2,30]. Further, the results obtained were compared with those obtained by high performance liquid chromatographic (HPLC) method [31]. These results indicated that the Nafion/ER-GO/GCE had high accuracy for detecting CA in commercial wine samples.

Table 1
Determination of CA in the white wine samples ($n=5$).

Wine samples (Brand name)	Analyte	Added (mg L^{-1})	Found Proposed method (mg L^{-1})	Found HPLC method (mg L^{-1})	Recovery
White wine A	Caffeic acid	–	2.99 ± 0.07	2.85 ± 0.02	–
		2	4.94		98
		4	6.86		98
	Chlorogenic acid	–	–	nd	
	Ferulic acid	–	–	2.55 ± 0.03	
	Gallic acid	–	–	2.07 ± 0.04	
	(+)-Catechin	–	–	10.16 ± 0.08	
White wine B	Caffeic acid	–	2.56 ± 0.08	2.47 ± 0.05	–
		2	4.49		97
		4	6.44		97
	Chlorogenic acid	–	–	nd	
	Ferulic acid	–	–	nd	
	Gallic acid	–	–	4.09 ± 0.04	
	(+)-Catechin	–	–	10.23 ± 0.06	

nd: not detected.

4. Conclusions

Nafion/ER-GO nanocomposite film modified electrode was prepared and utilized as electrochemical sensing interface for CA. The method was successfully applied to the quantitative determination of caffeic acid in white wine samples without interferences from other hydroxycinnamic acids (coumaric, sinapic

and ferulic acid) or ascorbic acid. The results indicated that the Nafion/ER-GO nanocomposite was an advantageous microenvironment for the electrochemical quantitative determination of CA. Nafion/ER-GO based electrochemical sensor possessed a lower detection limit, higher sensitivity and long-term stability for the determination of CA. Applicability of Nafion/ER-GO/GCE for quantitative determination of CA in commercial wines was also proved with satisfactory results.

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