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ORIGINAL ARTICLE

A comparison study of adsorptive transfer voltammetry and solution phase voltammetry for the determination of caffeic acid

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Abstract This study reports a comparison of adsorptive transfer and solution phase voltammetric methods for the study of caffeic acid. For this purpose, a platform was prepared by the modification of glassy carbon electrodes (GCEs) with MWCNTs and samarium nanoparticles (SmNPs) by means of an ultrasonic bath. The surface morphology of the platform was characterized using SEM, EDX and XRD. The adsorptive transfer voltammetric method was based on the adsorption of caffeic acid (CFA) at the surface of the modified electrode by keeping it into a solution of CFA. Afterwards, the modified electrode was transferred with the adsorbed species in a cell containing only 0.1 mol L^{-1} phosphate buffer solution (PBS) for the analysis. The current response of CFA was found to be linear over a concentration from 5.0×10^{-10} mol L^{-1} to 1.0×10^{-7} mol L^{-1}. The values of the limit of detection (LOD) and limit of quantification (LOQ) were 2.0×10^{-10} mol L^{-1} and 6.67×10^{-10} mol L^{-1}, respectively. The adsorptive transfer method using the modified electrode (SmNPs/MWCNTs/GCE) has successfully been applied to food samples for determining CFA. The solution phase voltammetry was carried out by dipping the electrode into a voltammetric cell containing CFA. The plot of peak currents was linear over the concentration range of 5.0×10^{-9} mol L^{-1} –8.0×10^{-8} mol L^{-1}. The values of LOD and LOQ were 2.0×10^{-9} mol L^{-1} and 6.67×10^{-9} mol L^{-1} for CFA using a classical solution phase voltammetry at the proposed platform. It was shown that the LOD obtained at adsorptive transfer voltammetry was 10-fold lower when compared to classical solution phase voltammetry.

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1. Introduction

Caffeic acid (CFA), a phenolic compound, is naturally present in spices, herbs and seeds. It serves as an antioxidant and available in drinks and other food samples including wine,

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tea, coffee, olive oil (Sun et al., 2018). CFA has also antioxidant, anti-inflammatory, antibacterial, anticarcinogenic and immunomodulatory properties (Aguilar-Hernández et al., 2017; Manikandan et al., 2018). More recently, a comprehensive study has revealed that CFA could block HIV replication with moderate anti-HIV activity in cell cultures (Sonar et al., 2017). Thus, a sensitive determination of CFA is of importance for analytical and therapeutic interests as well as safety and quality of food samples. Recently, a number of methods including capillary electrophoresis, spectrophotometry and chromatography were appeared for the determination of CFA herbs and wine samples (Wang et al., 2004; Aguilar-Hernández et al., 2017; Şanli et al., 2016). However, these methods suffer from a number of disadvantages including time consuming steps for derivatization or extraction steps. However, voltammetric techniques enable rapid analysis on food samples with high precision and accuracy (Bianchini et al., 2014; Liu et al., 2016a; Zhang et al., 2013; Chen et al., 2019; Filik et al., 2013; Gao et al., 2018). Voltammetric behavior of CFA has been reported and its mechanism has been studied (Robledo et al., 2016; Trabelsi et al., 2004; Karabozhikova and Tsakova, 2019). Different electrochemical methods have been developed for the determination of CFA in in wine, tea, coffee, olive oil, juice, plants and pharmaceuticals (Ciepiela et al., 2016; Vilian et al., 2014; Fernandez et al., 2018; Velmurugan, 2017; Tyszczuk et al., 2011; Li et al., 2017). Various electrode materials such as carbon nanotubes, r-GO, graphite, carbon black, polymers, chitosan, graphene and metallic nanoparticles were utilized for the determination of CFA (Shi et al., 2018; Titretir Duran et al., 2017; David et al., 2015; Thangavelu et al., 2017; Jing et al., 2017; Sakthinathan et al., 2017; Pandian et al., 2019; Zhao et al., 2019; Karabiberoğlu et al., 2013; Liu et al., 2016b). However, previous studies revealed that the electrochemical platforms based on carbon nanotubes and metallic/metallic oxide nanoparticles exhibited excellent reproducibility and low detection limits for various species in electroanalysis (Wang et al., 2016; Messaoud et al., 2017). For instance, Guo et al. have presented a voltammetric procedure based on gold nanoparticles and multi-walled carbon nanotubes as an enhanced material for the sensitive detection of tryptophan and a nano-molar level of detection was reported (Guo et al., 2010). A modified electrode constructed with carbon nanotubes and zinc oxide has appeared in the literature for the sensitive detection of citalopram (Ghaedi et al., 2016). Sunder and co-workers have also developed an electrochemical method based on graphene oxide/yttrium oxide modified glassy carbon electrode for the selective determination of L-DOPA (Sunder et al., 2019). In addition, it has been reported that samarium oxide exhibited excellent catalytic activity and high conductivity (Gao et al., 2002; Constantinescu et al., 2012). Samarium nanoparticles also provide thermal and chemical stability, as well as considerable surface area when used in composite electrodes (Dezfuli et al., 2017). In this study, a voltammetric sensing platform based on modifying glassy carbon electrodes (GCEs) with multi-walled carbon nanotubes (MWCNTs) and samarium nanoparticles (SmNPs) was prepared using an ultrasonic bath. Then, the proposed platform (SmNPs/MWCNTs/GCE) was utilized for a comparison of adsorptive transfer voltammetric method and classical solution phase voltammetry for the study of CFA. The adsorptive transfer voltammetric method was successfully applied for the determination of CFA in various food samples such as coffee, tea and herbals.

2. Experimental

2.1. Chemicals

Caffeic acid (CFA), uric acid (UA), ascorbic acid (AA), paracetamol (PAR) and tryptophan (TRP) were all purchased from Sigma-Aldrich Chemical Company (Germany). Multi-walled carbon nanotubes and samarium oxide powder (15–45 nm) were obtained from US-Nano Materials Company (USA). Acetone, ethanol, chloroform, nitric acid, perchloric acid, disodium hydrogen phosphate and potassium dihydrogen phosphate obtained from Merck (Germany) were of analytical grade. Samples of clove buds, cinnamon, ginger, turmeric, Turkish coffee, Turkish black tea, Turkish green tea and rosehip were purchased from a local store. Caffeic acid tablets were kindly obtained from a local herbal product and vitamins shop. Stock solutions of CFA, UA, TRP, PAR and AA were prepared using 0.1 mol L^{-1} phosphate buffer solution (PBS). Ultrapure water was used for the preparation of phosphate buffer. Oxygen-free nitrogen was bubbled through the voltammetric cell prior to each measurement.

2.2. Instrumentation

Voltammetry was performed using an Ecochemie Autolab PGSTAT-12 potentiostat/galvanostat (Netherlands). Glassy carbon electrodes (GCEs) with 3 mm in diameter (Bioanalytical Systems, USA) served as working electrodes. Ag/AgCl in 3 mol L^{-1} KCl was used as a reference electrode while a Pt rod served as auxiliary electrode in voltammetric measurements. Both reference and counter electrodes were purchased from Metrohm (Switzerland). A Metrohm brand pH meter was utilized for pH measurements. Images of scanning electron microscopy (SEM) and the spectrum of energy dispersive X-ray analysis (EDX) were performed on Zeiss EVO 50 Research Grade Variable Pressure Scanning Electron Microscope (USA). The pattern of X-ray diffraction (XRD) was recorded on Rigaku Ultima III X-ray Diffractometer (USA).

2.3. SmNPs/MWCNTs/GCE platform preparation

Glassy carbon electrodes (GCEs) were polished on a pad with 1 μm and 0.3 μm alumina powders. Then, the GCEs were subjected to sonication for 5 min in ethanol and then rinsed with ultra-pure water. The GCEs were then activated in a voltammetric cell containing 0.1 mol L^{-1} PBS in a large potential window at a scan rate of 100 mV/s by cyclic voltammetry (CV). MWCNTs were subjected to sonication in a mixture of 7:3 ratio (v/v) of HNO_3 and $HClO_4$ for 5 h. 5 mg MWCNTs and 1 mg Sm were weighed and placed in a flask containing 10 mL chloroform and kept under sonicaation for 45 min. Finally, 5 μL of suspension of SmNPs/MWCNTs was pipetted and then placed on GCE surface. Then, the modified electrode was dried under pure nitrogen gas. The proposed platform was denoted as SmNPs/MWCNTs/GCE and washed with ultrapure water before use. The modified electrode (SmNPs/MWCNTs/GCE) was then subjected to activation by CV in

an electrochemical cell at a potential range from −0.4 to +1.0 V at a scan rate of 100 mV/s. The preparation of SmNPs/MWCNTs/GCE and the measurement have been illustrated in Scheme 1.

2.4. Optimization of adsorption time

Voltammetry of CFA exhibited that an optimal ratio of 5:1 of the mixture of multi-walled carbon nanotubes and SmNPs was appropriate for determining CFA with the lowest peak potential separation (Fig. 1A). In addition, the results showed that 5 μL of composite suspension was appropriate to improve the response for CFA (Fig. 1B). The highest current response with good precision was obtained using 5 μL of composite suspension. A plot of peak current versus time for the adsorption of 2.0×10^{-8} mol L^{-1} CFA at the proposed platform is given in Fig. 1C. It was concluded that the adsorption was completed after 10 min of dipping the proposed platform into a solution containing CFA

2.5. Voltammetric measurements

The proposed platform (SmNPs/MWCNTs/GCE) was placed in an electrochemical cell containing 0.1 mol L^{-1} PBS at pH 7.0 for the activation of its surface by cyclic voltammetry. In adsorptive transfer voltammetric method, CFA was adsorbed at modified electrode after keeping it into a solution of CFA for 10 min. Afterwards, electrodes were washed with ultrapure water and transferred in a voltammetric cell containing only a buffer solution for the voltammetric analysis. Cyclic voltammograms were obtained at GCE, MWCNTs/GCE and SmNPs/MWCNTs/GCE for a comparison. The mechanism of CFA at SmNPs/MWCNTs/GCE was obtained using cyclic voltammetry at various scan rates. Voltammetry was performed in buffer solutions at various pH values to determine the number of proton transferred in the electrode reaction of CFA. Square wave voltammetry was then performed to obtain the linear current-concentration equation for CFA. Prior to the voltammetric analysis, CFA was extracted from food samples. Solution phase voltammetry was carried out by dipping the modified electrode into an electrochemical cell containing CFA.

2.6. Sample preparation

Prior to the voltammetric analysis, CFA was extracted from food samples such as clove buds, cinnamon, ginger, turmeric, Turkish coffee, Turkish black tea, Turkish green tea and rosehip. For this purpose, 0.5 g of each sample was weighed and then placed into a flask and diluted with methanol. Then, it was diluted with 0.1 mol L^{-1} PBS at pH 7.0, the adjustment of pH was carried out using HCl or NaOH. Afterwards, it was sonicated in an ultrasonic bath for 10 min followed by stirring for over 2 h. Then, each sample was filtered to remove any solid. Then, a known volume of the supernatant was added to a beaker containing 50 mL of 0.1 mol L^{-1} PBS at pH 7.0. The modified electrode was then kept in a solution of the food sample for 10 mins. Afterwards, the modified electrode was rinsed with water and transferred into a voltammetric cell containing 0.1 mol L^{-1} PBS at pH 7.0, and then the voltammetric analysis was performed. Then, standard addition method was applied for the recovery of CFA in each food sample. Also, five caffeic acid tablets (each containing 300 mg CFA) were weighed and crushed in a mortar. Then, an appropriate amount was dissolved in a 25 mL of 0.1 mol L^{-1} PBS at pH 7.0. Afterwards, an appropriate volume of supernatant was transferred into a beaker containing 50 mL of 0.1 mol L^{-1} PBS at pH 7.0. Then, the analysis was performed for the determination of CFA in tablets.

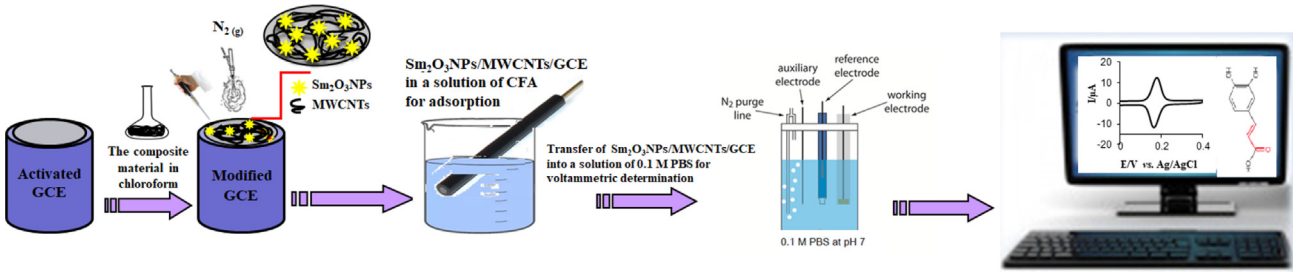
3. Results and discussion

3.1. Characterization of platform material

The characterization of SmNPs/MWCNTs was performed by scanning electron microscopy (SEM). Fig. 2A exhibits an image for SmNPs/MWCNTs. Data revealed the dispersion of Sm nanoparticles on MWCNTs. The energy dispersive X-ray analysis (EDX) is given in Fig. 2B. The data showed that Sm, C, Au and Pd were exhibited in a spectrum of EDX. Au and Pd were appeared due to the gold coating before the SEM measurements. The XRD spectrum of the electrode material was presented in Fig. 2C. The peak exhibited at 26° is due to the hexagonal structure of MWCNTs. However, the other peaks located at 2θ = 32°, 36°, 52° and 62° can be assigned to samarium.

3.2. Voltammetric behaviour of caffeic acid

Typical background cyclic voltammograms of unmodified GCE (a), GCE modified with MWCNTs (b) and GCE modified with a composite of SmNPs/MWCNTs (c) in 0.1 mol L^{-1} PBS at pH 7.0 are presented in Fig. 3A. No peaks are observed in the absence of CFA. However, adsorptive transfer cyclic voltammetry was performed to examine the electrode behaviour of CFA at different electrodes. Firstly, CFA was



Scheme 1 A schematic preparation of the platform and the study of caffeic acid.

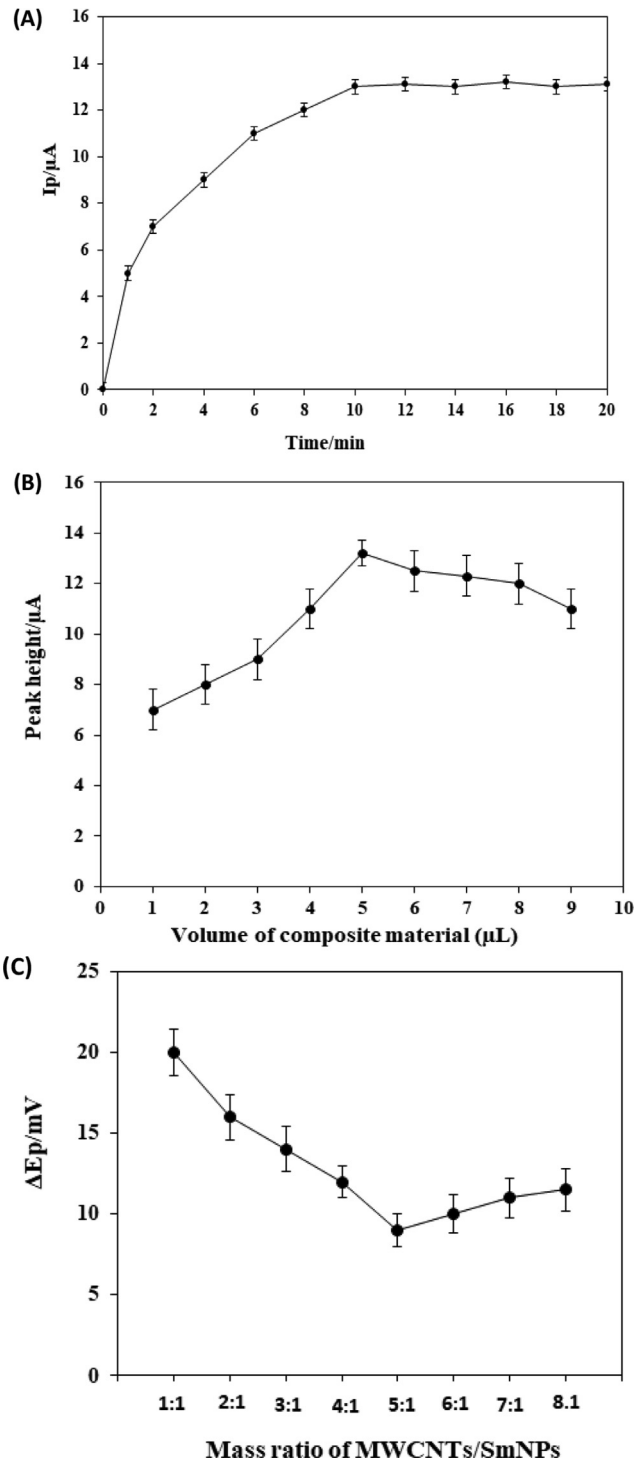


Fig. 1 A plot of peak currents versus adsorption time for 2.0×10^{-8} mol L^{-1} CFA (A). A plot of peak current versus the volume of composite material for the adsorption of 2.0×10^{-8} mol L^{-1} CFA (B). A plot of the separation in the peak potential versus the mass ratio for the adsorption of 2.0×10^{-8} mol L^{-1} CFA (C).

adsorbed at modified electrode surface by keeping the electrode into a solution of CFA for 10 min. Then, the modified electrode was washed with ultra-pure water and transferred with the adsorbed species in a voltammetric cell containing 0.1 mol L^{-1} PBS at pH 7.0, and then the voltammetry was performed in this medium. Cyclic voltammograms of CFA at GCE (a), MWCNTs/GCE (b) and SmNPs/MWCNTs/GCE (c) are given in Fig. 3B. As shown, no peaks were appeared at unmodified GCE (voltammogram a). Meanwhile, MWCNTs/GCE exhibited an oxidation peak at 0.186 V and a reduction peak at 0.173 V. ΔE_p was about 13 mV for CFA at MWCNTs/GCE as given in Fig. 3B (voltammogram b). The SmNPs/MWCNTs/GCE system exhibited a sharp, an improved and a well-defined oxidation peak at 0.174 V and a reduction peak at 0.165 V with an ΔE_p of 9 mV for the two electron process of the redox couple of CFA as shown in Fig. 3B (voltammogram c). The ratio of anodic and cathodic peak currents was close to 1 for the redox process of CFA. In addition, the peak separation was decreased to 9 mV at the surface of SmNPs/MWCNTs/GCE. The observation of the decrease in ΔE_p at SmNPs/MWCNTs/GCE system was an evidence of the acceleration of the redox process. The voltammetric platform has also enhanced current response of CFA in comparison with MWCNTs/GCE. Experimental results showed that the SmNPs/MWCNTs/GCE system was more appropriate for the voltammetric studies of CFA as the proposed platform exhibited decreased overpotential, good catalytic effect, large current response and the decrease in ΔE_p for CFA. The increase in current intensities is probably related to the increase of the electroactive area of the electrode promoted by samarium nanoparticles.

Various scan rates were applied to the cyclic voltammetry of CFA to acquire the possible electrode mechanism (Fig. 4). The peak current was linear with scan rates over a range from 25 to 200 mV/s. This behaviour indicated that the electrode process of CFA at the SmNPs/MWCNTs/GCE system was surface-controlled. In addition, the ratio of peak currents was maintained and no shifts were observed in anodic and cathodic peak potentials of CFA with increasing scan rates. Thus, the separation in peak potentials of CFA was constant at increasing scan rates. This indicated a reversible redox behaviour for the electrode process of CFA using the adsorptive transfer voltammetry at the proposed platform (Elgrishi et al., 2018). In addition, cyclic voltammograms of CFA at various scan rates using a classical voltammetric method are presented in Fig. 4B. As clearly seen that peak potentials are shifted with increase in scan rate and consequently ΔE_p increases. This shows that the reversibility of CFA is not maintained using a classical voltammetric method at the proposed electrode. The adsorptive transfer voltammetric procedure was also performed for the investigation of the influence of solution pH on Ep of 1.0×10^{-8} mol L^{-1} CFA. The voltammograms at different pH values are given in Fig. 5A. The shifts in peak potentials with the change in pH clearly indicate that a number of protons are transferred accompanying electrons. The slope of the plot of Ep versus pH was −61.8 mV pH^{-1} indicated that the ratio of the number of protons and the number of electrons was 1:1 in the process of CFA. These results reveal that the reaction of CFA undergoes with two protons as two electrons are transferred in the electrode process as shown in Scheme 2 (Gao et al., 2018).

In addition, cyclic voltammograms of 1.0×10^{-8} mol L^{-1} CFA at various pH values using the classical solution phase voltammetry are given in Fig. 5B. A slope was −62.1 mV pH^{-1} was obtained in classical solution phase voltammetry. Different current values were obtained using the classical

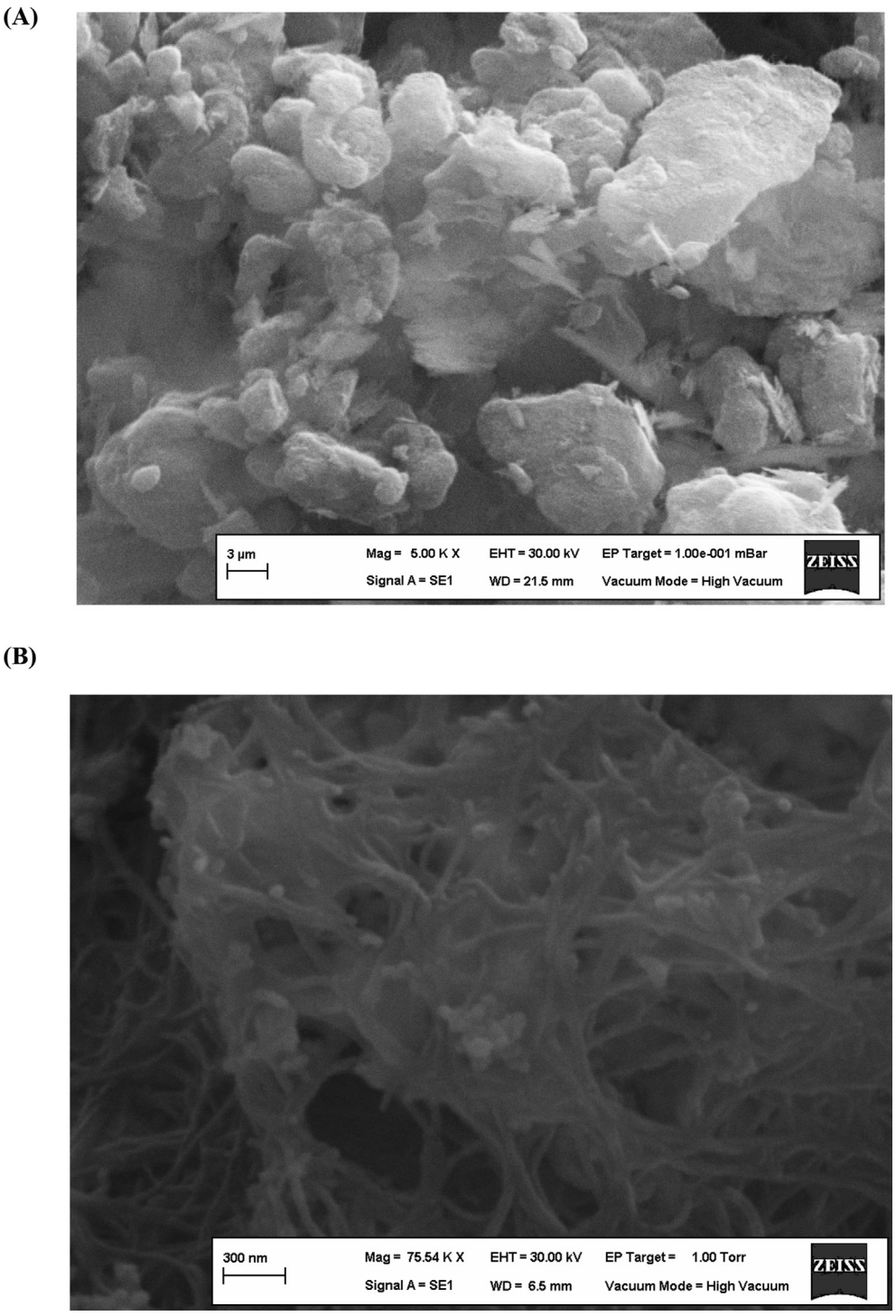


Fig. 2 The SEM image (A), EDX spectrum (B) and the XRD pattern (C) of SmNPs/MWCNTs.

solution phase voltammetry for the pH studies of CFA when compared to the current response obtained by the adsorptive transfer voltammetry.

3.3. Determination of caffeic acid

The adsorptive transfer voltammetry at the SmNPs/MWCNTs/GCE system was performed to obtain a calibration plot for CFA. Square wave voltammograms of various concentrations of CFA are given in Fig. 6A. A plot of anodic currents versus concentrations was linear over the range of 5.0×10^{-10} mol L^{-1} –1.0×10^{-7} mol L^{-1} (Fig. 6B). A detection limit (LOD) of 2.0×10^{-10} mol L^{-1} was obtained. The detection limit was calculated based on $3S_b/m$ where S_b was the standard deviation of blank and m was the slope of Fig. 6B. The results yielded a linear equation of Ip(µA) = 1.0277C(nmol L^{-1}) + 0.1328 with a correlation coefficient of 0.9990. A comparison of the proposed electrode with previ-

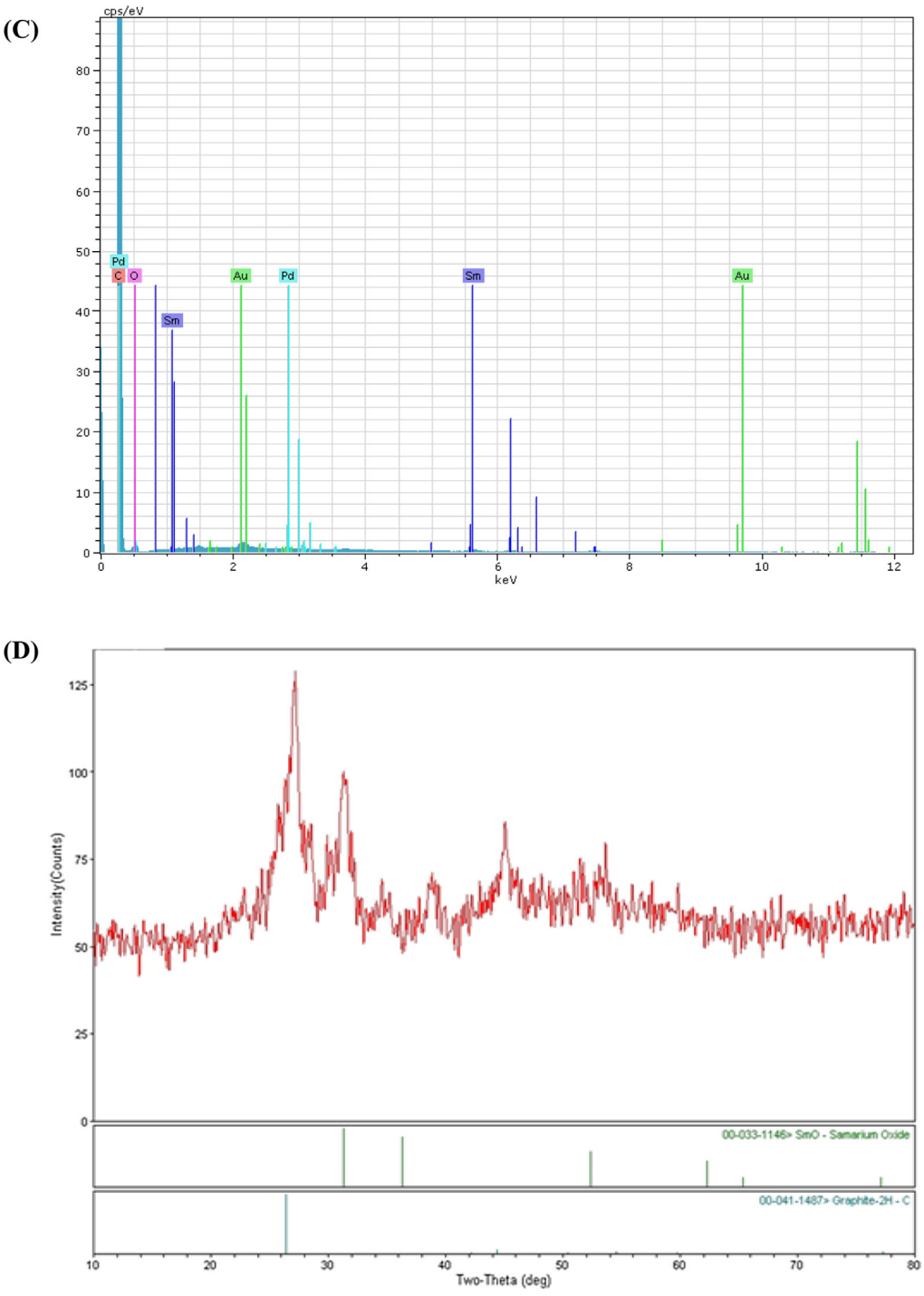


Fig. 2 (*continued*)

ously published electrodes in LOD point of view is presented in Table 1. The results yielded a limit of quantification (LOQ) of 6.67×10^{-10} mol L^{-1}. The experimental results indicate that the adsorptive transfer voltammetry with the proposed electrode enables a lower detection limit and is well compared to the previously published results for the detection of CFA (Jing, 2017; Karikalan et al., 2017; Karthik et al., 2017; Sivasankar et al., 2018; Liu et al., 2016a; Karabiberoğlu et al., 2013; Tyszczuk et al., 2011; Zhang et al., 2013). The performance of the adsorptive transfer voltammetry was also compared with a classical solution phase voltammetry for the determination of CFA. Square wave voltammograms of various concentration of CFA using a classical solution phase voltammetry are given in Fig. 6C. The plot of peak currents was linear over the range of 5.0×10^{-9} mol L^{-1} –8.0×10^{-8} mol L^{-1} (Fig. 6D). The values of LOD and LOQ were 2.0×10^{-9} mol L^{-1} and 6.67×10^{-9} mol L^{-1} for CFA using a classical solution phase voltammetry at the proposed platform. The

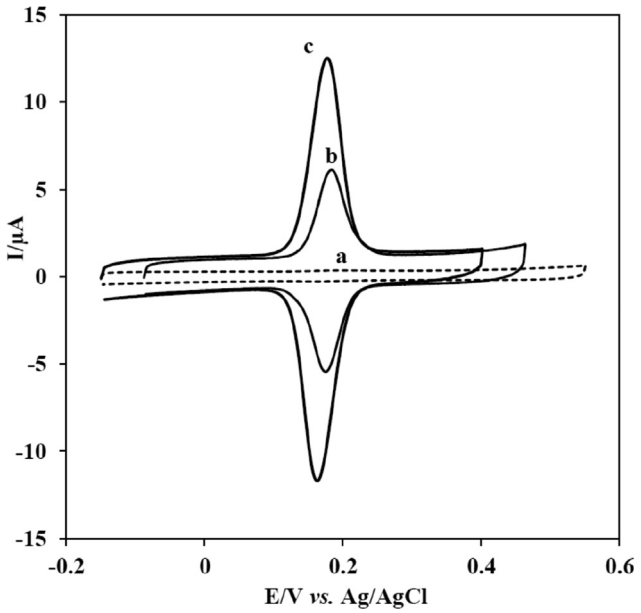


Fig. 3 (A) Cyclic voltammograms of 1.0×10^{-8} mol L^{-1} CFA at bare GCE (a), MWCNTs/GCE (b) and SmNPs/MWCNTs/GCE (c) in 0.1 M PBS at pH 7.0. Scan rate: 50 mV/s.

results clearly indicated that the performance of the proposed adsorptive transfer voltammetric method was excellent and much superior when compared to a classical solution phase voltammetry.

3.4. Repeatability, stability and selectivity

Adsorptive transfer cyclic voltammetry was performed to study the repeatability of the proposed voltammetric platform. For this purpose, repetitive voltammograms of CFA were recorded (Fig. 7A). The results showed that the decrease in the current response of CFA was almost negligible. The results yielded a relative standard deviation (RSD) of 0.1% for the 10 repetitive runs for 5 nmol L^{-1} CFA indicated that the repeatability of the proposed adsorptive transfer voltammetric method with the proposed modified electrode was excellent. Cyclic voltammograms of repetitive runs for 5 nmol L^{-1} CFA using the classical voltammetric procedure are presented in Fig. 7B. The RSD was 5.6% for CFA using the classical method. This indicated that the repeatability of the proposed adsorptive transfer method is superior when compared to a classical voltammetric procedure. In addition, the RSD% of three different electrodes was only 4.2%. The results indicated that both reproducibility and repeatability was excellent for CFA using the adsorptive transfer voltammetry at SmNPs/MWCNTs/GCE.

The stability of SmNPs/MWCNTs/GCE was examined in PBS for 15 days. The decrease of the response of CFA was less than 7–8%. Such a slight decrease in current response of CFA indicated good stability of SmNPs/MWCNTs/GCE by the adsorptive transfer voltammetric method. The results showed that citric acid, lactic acid and glucose had no remarkable influence on the behaviour and determination of CFA. This indicated that the selectivity of the adsorptive transfer

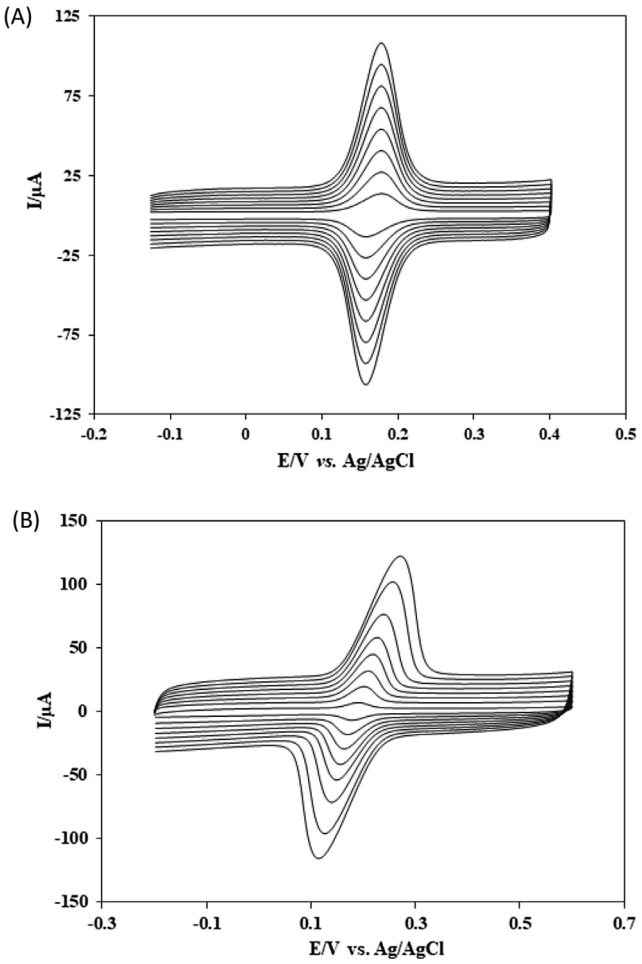


Fig. 4 (A) Cyclic voltommograms of 1.0×10^{-8} mol L^{-1} CFA at SmNPs/MWCNTs/GCE in 0.1 mol L^{-1} PBS at pH 7.0. Scan rates increasing from 25 mV/s to 200 mV/s. (B) Classical solution phase cyclic voltommograms of 1.0×10^{-8} mol L^{-1} CFA at SmNPs/MWCNTs/GCE in 0.1 mol L^{-1} PBS at pH 7.0. Scan rates increasing from 25 mV/s to 200 mV/s.

voltammetric method at SmNPs/MWCNTs/GCE was excellent. Furthermore, square wave voltammograms of various concentrations of CFA in the presence of 2.0×10^{-5} mol L^{-1} ascorbic acid (AA) are shown in Fig. 7C. The results indicate no interference of AA on the electrode process of CFA at SmNPs/MWCNTs/GCE. A plot of peak currents versus the concentration of CFA in the presence of 2.0×10^{-5} mol L^{-1} AA is given in Fig. 7D. A linear equation of Ipa(μA) = 1.0442C(nmol L^{-1}) + 0.063 (R^2 = 0.9982) was obtained in the presence of AA. This shows that the slope of external calibration is similar to the slope obtained in the presence of AA. The values of LOD and LOQ were calculated as 1.97×10^{-10} mol L^{-1} and 6.6×10^{-10} mol L^{-1} for CFA in the presence of AA. Data indicated that the sensitive determination of CFA was also possible in the presence of AA. Also, a square wave voltammogram of the mixture of 1.0×10^{-5} mol L^{-1} AA, 3.0×10^{-9} mol L^{-1} CFA, 1.0×10^{-5} mol L^{-1} uric acid (UA), 1.0×10^{-7} mol L^{-1} paracetamol (PAR) and 1.0×10^{-6} mol L^{-1} tryptophan (TRP) is given in Fig. 7E. The modified electrode exhibited four well-defined anodic

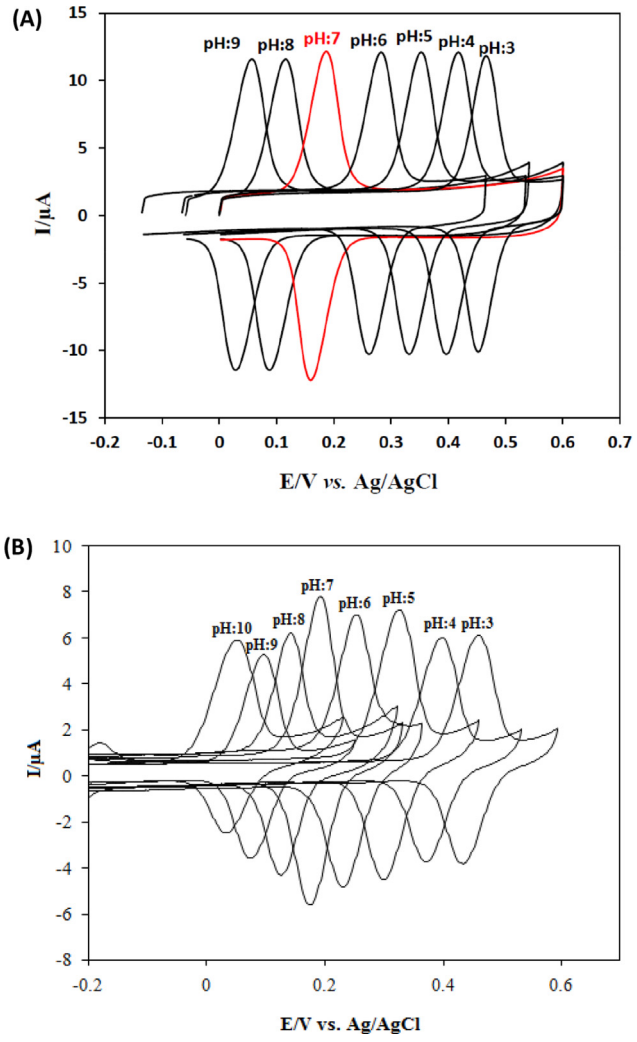


Fig. 5 (A) CVs of 1.0×10^{-8} mol L^{-1} CFA at SmNPs/MWCNTs/GCE in 0.1 mol L^{-1} PBS at various pH values. Scan rate: 50 mV/s. (E) A plot of anodic peak potentials of CFA vs pH. (F) Cyclic voltammograms of 1.0×10^{-8} mol L^{-1} CFA at various pH values using the classical solution phase voltammetry. Scan rate: 50 mV/s.

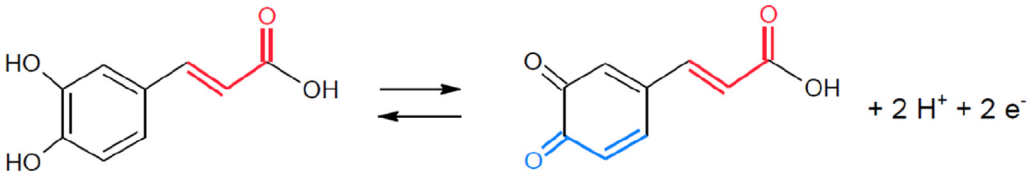
peaks at −0.03 V, 0.18 V, 0.31 V, 0.39 V and, 0.70 V for AA, CFA, UA, PAR and TRP respectively. In addition, Fig. 6D shows increasing concentrations of AA, CFA, UA, PAR and TRP using the proposed method. It is clear that different molar ratios of AA, UA, PAR and TRP have no influence on the determination of CFA. This clearly shows that the selectivity of proposed adsorptive transfer voltammetric method at SmNPs/MWCNTs/GCE is excellent and the procedure can be successfully applied for the determination of CFA in mixtures.

3.5. Determination of caffeic acid in food samples

The adsorptive transfer voltammetry at SmNPs/MWCNTs/GCE was performed for the determination of CFA in several food samples such as clove buds, cinnamon, ginger, turmeric, Turkish coffee, Turkish black tea, Turkish green tea and rosehip. The results are presented in Table 2. The total amount of CFA determined at SmNPs/MWCNTs/GCE in each sample was referred to the regression equation obtained in the calibration study. Recovery values were obtained by the addition of a known amount of CFA standard solutions to the food samples. The recoveries were between 97.0% and 101.0%. The accuracy of the proposed method was also assured for the determination of CFA in tablets (Table 3). A mean recovery of %97.5 with an RSD% of 2.8% was obtained for the analysis of tablets. The reasonable values of recoveries and RSDs % calculated at the proposed voltammetric platform demonstrate that the adsorptive transfer voltammetric method of analysis is accurate and precise for determining CFA.

4. Conclusions

A comparison of adsorptive transfer and solution phase voltammetric methods for the study of CFA was carried out. For this purpose, a voltammetric sensing platform was prepared by the modification of glassy carbon electrodes (GCEs) with multi-walled carbon nanotubes (MWCNTs) and samarium nanoparticles (SmNPs) by means of an ultrasonic bath. The solution phase voltammetry was carried out by dipping the modified electrode into a voltammetric cell containing CFA. The plot of peak currents was linear over the range of 5.0×10^{-9} mol L^{-1} –8.0×10^{-8} mol L^{-1}. The values of LOD and LOQ were 2.0×10^{-9} mol L^{-1} and 6.67×10^{-9} mol L^{-1} for CFA using a classical solution phase voltammetry at the proposed platform. In case of adsorptive transfer voltammetry, CFA was adsorbed at the surface of the proposed voltammetric platform by keeping it into a solution of CFA. Then, the platform was transferred with the adsorbed species in an electrochemical cell containing only 0.1 mol L^{-1} phosphate buffer solution (PBS) for the voltammetric analysis. The current response of CFA was found to be linear over a concentration from 5.0×10^{-10} mol L^{-1} to 1.0×10^{-7} mol L^{-1} with a detection limit of (LOD) of 2.0×10^{-10} mol L^{-1}. The LOQ was calculated as 2.0×10^{-10} mol L^{-1}. The modified electrode (SmNPs/MWCNTs/GCE) has successfully been applied to various food samples for the determination of CFA. It was shown that the LOD obtained at adsorptive transfer voltammetry was 10-fold lower than that calculated at classical solution phase voltammetry.



Scheme 2 Possible electron transfer reaction at the proposed platform.

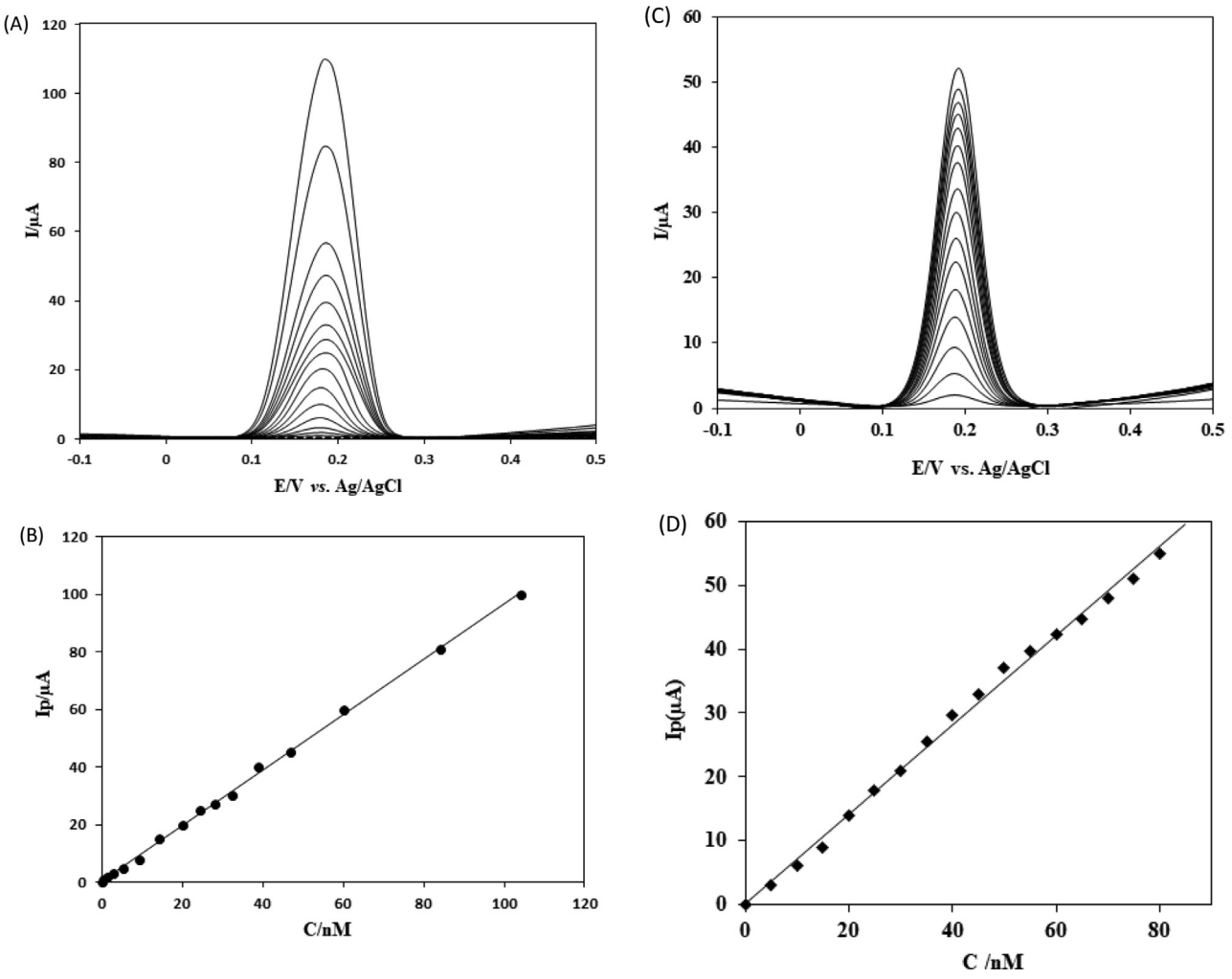


Fig. 6 (A) Square wave voltammograms (SWVs) of various CFA concentrations at SmNPs/MWCNTs/GCE in 0.1 mol L^{-1} PBS at pH 7.0. Frequency: 20 Hz. Step potential: 5 mV. Amplitude: 20 mV. CFA concentrations: 0.0 mol L^{-1}; 5.0×10^{-10} mol L^{-1}; 1.0×10^{-9} mol L^{-1}; 2.0×10^{-9} mol L^{-1}; 3.0×10^{-9} mol L^{-1}; 5.0×10^{-9} mol L^{-1}; 9.0×10^{-9} mol L^{-1}; 1.5×10^{-8} mol L^{-1}; 2.0×10^{-8} mol L^{-1}; 2.2×10^{-8} mol L^{-1}; 2.7×10^{-8} mol L^{-1}; 4.0×10^{-8} mol L^{-1}; 4.5×10^{-8} mol L^{-1}; 6.0×10^{-8} mol L^{-1}; 8.0×10^{-8} mol L^{-1}; 1.0×10^{-7} mol L^{-1}. (B) A plot of peak currents against the concentrations of CFA. (C) Classical solution phase square wave voltammograms (SWVs) of various CFA concentrations at SmNPs/MWCNTs/GCE in 0.1 mol L^{-1} PBS at pH 7.0. Frequency: 20 Hz. Step potential: 5 mV. Amplitude: 20 mV. CFA concentrations: 0.0 mol L^{-1}; 5.0×10^{-9} mol L^{-1}; 1.0×10^{-8} mol L^{-1}; 1.5×10^{-8} mol L^{-1}; 2.0×10^{-8} mol L^{-1}; 2.5×10^{-8} mol L^{-1}; 3.0×10^{-8} mol L^{-1}; 4.0×10^{-8} mol L^{-1}; 4.5×10^{-8} mol L^{-1}; 5.0×10^{-8} mol L^{-1}; 5.5×10^{-8} mol L^{-1}; 6.0×10^{-8} mol L^{-1}; 6.5×10^{-8} mol L^{-1}; 7.0×10^{-8} mol L^{-1}; 7.5×10^{-8} mol L^{-1}; 8.0×10^{-8} mol L^{-1}. (D) A plot of peak currents against the concentrations of CFA using the solution phase voltammetry.

Table 1 A comparison of the proposed electrode with published electrodes for the determination of CFA.

Electrode	Technique	Linear range (mol L^{-1})	Detection limit (mol L^{-1})	Reference
Pd-Au-PEDOT-graphene/GCE	DPV	1.0×10^{-9}–5.5×10^{-7}	3.7×10^{-10}	(Liu et al., 2016a)
Ag-poly(thiophene)/GCE	DPV	1.0×10^{-8}–4.3×10^{-6}	5.3×10^{-9}	(Karabiberoğlu et al., 2013)
Pd-film/GCE	SWV	1.0×10^{-8}–5.0×10^{-7}	4.0×10^{-9}	(Tyszczuk et al., 2011)
g-C_3N_4/chitosan/GCE	DPV	5.5×10^{-6}–1.6×10^{-4}	1.9×10^{-6}	(Jing et al., 2017)
SrV_2O_6/GCE	Amperometry	1.0×10^{-8}–2.07×10^{-4}	4.0×10^{-9}	(Karthik et al., 2017)
HMGO/GCE	Amperometry	1.0×10^{-8}–6.08×10^{-4}	4.0×10^{-9}	(Sivasankar et al., 2018)
Au-graphene/GCE	SWV	5.0×10^{-7}–5.0×10^{-5}	5.0×10^{-8}	(Zhang et al., 2013)
NDC/GCE	DPV	1.0×10^{-8}–3.5×10^{-4}	2.4×10^{-9}	(Karikalan et al., 2017)
SmNPs/MWCNTs/GCE	SWV	5.0×10^{-10}–1.0×10^{-7}	2.0×10^{-10}	This work

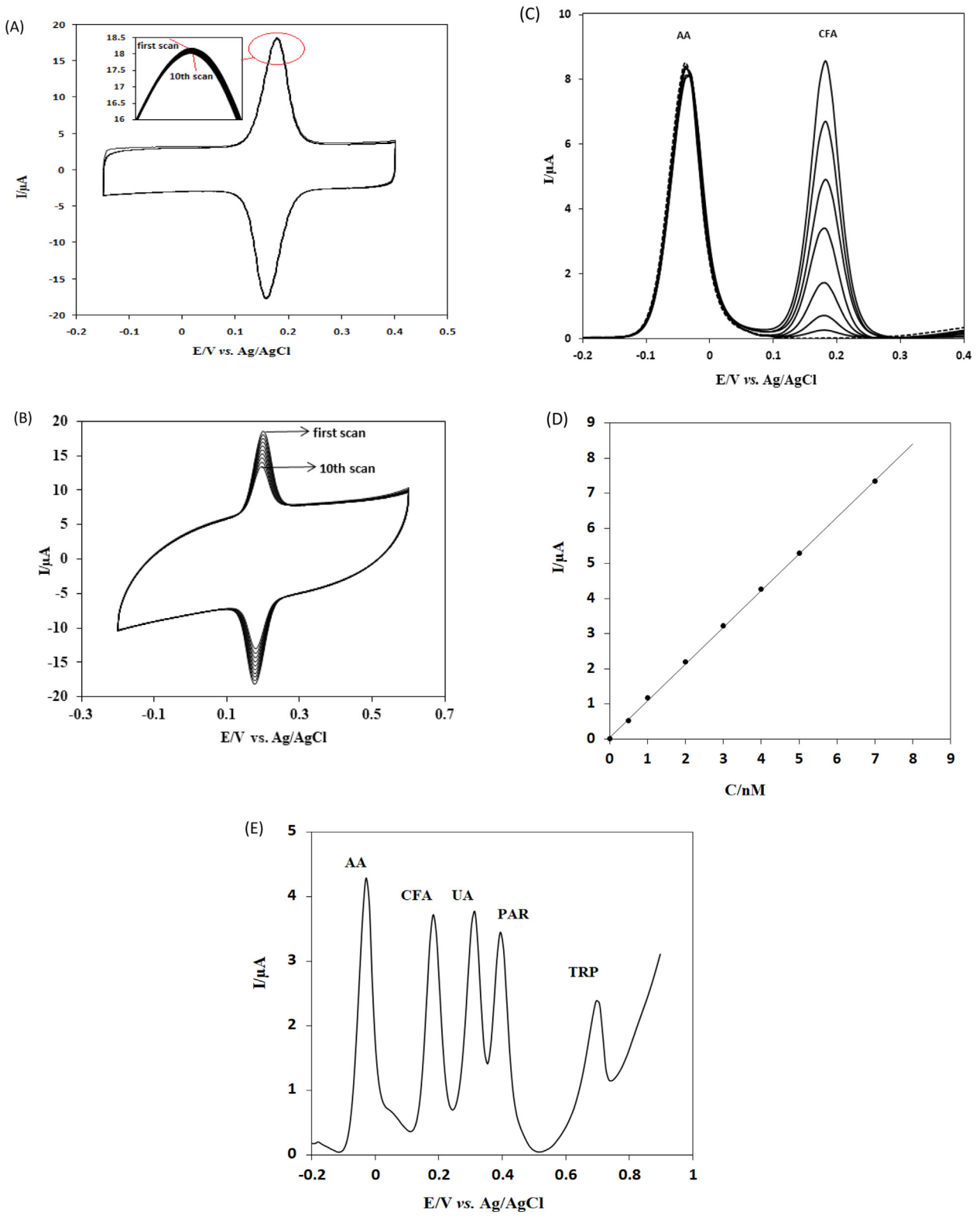


Fig. 7 (A) Repetitive adsorptive transfer cyclic voltammograms of CFA. Scan rate: 100 mV/s. (B) Repetitive classical solution phase cyclic voltammograms of CFA. Scan rate: 100 mV/s. (C) SWVs of increasing concentrations of CFA in the presence of 2.0×10^{-5} mol L^{-1} AA at SmNPs/MWCNTs/GCE in 0.1 mol L^{-1} PBS at pH 7.0. CFA concentrations: 0.00 mol L^{-1}; 5.0×10^{-10} mol L^{-1}; 1.0×10^{-9} mol L^{-1}; 2.0×10^{-9} mol L^{-1}; 3.0×10^{-9} mol L^{-1}; 4.0×10^{-9} mol L^{-1}; 5.0×10^{-9} mol L^{-1}; 7.0×10^{-9} mol L^{-1}. Scan rate: 50 mV/s. (D) A plot of peak currents versus the concentration of CFA. (E) SWVs of 1.0×10^{-5} mol L^{-1} AA, 3.0×10^{-9} mol L^{-1} CFA 1.0×10^{-5} mol L^{-1} UA, 1.0×10^{-7} mol L^{-1} PAR and 1.0×10^{-6} mol L^{-1} TRP at SmNPs/MWCNTs/GCE in 0.1 mol L^{-1} PBS at pH 7.0. Frequency: 20 Hz, Step potential: 5 mV, Amplitude: 20 mV.

Table 2 Voltammetric analysis of various food samples for the determination of CFA.

Sample	Added (nmol L^{-1})	Expected (nmol L^{-1})	Found (nmol L^{-1})	Recovery%	RSD%
Clove buds	–	–	2.5	–	2.4
	5	7.5	7.3	97.3	2.8
	10	12.5	12.3	98.4	2.6
	20	22.5	22.2	98.5	2.3
Cinnamon	–	–	9.7	–	3.0
	10	19.7	18.8	95.3	3.1
	20	20.7	28.6	96.2	2.8
	40	49.7	48.4	97.3	2.5
Ginger	–	–	3.9	–	3.1
	4	7.9	7.7	97.5	3.3
	8	11.9	11.7	98.0	2.8
	16	19.9	20.1	101.0	2.5
Turmeric	–	–	8.5	–	2.9
	10	18.5	18.1	98.0	3.0
	20	28.5	28.1	98.3	2.6
	40	48.5	47.8	98.6	2.2
Turkish coffee	–	–	15.2	–	2.0
	15	30.2	29.9	99.0	2.6
	30	45.2	44.6	98.7	2.4
	60	75.2	74.4	99.0	2.2
Turkish black tea	–	–	4.8	–	2.5
	5	9.8	9.7	97.0	2.3
	10	14.8	14.5	98.0	2.1
	20	24.8	24.4	98.5	2.0
Turkish green tea	–	–	5.1	–	2.5
	5	10.1	9.8	97.0	3.0
	10	15.1	14.8	98.0	2.7
	20	25.1	24.9	99.2	2.2
Rosehip	–	–	7.3	–	3.0
	10	17.3	16.9	97.8	3.0
	20	27.3	26.8	98.0	2.5
	30	37.3	36.5	97.9	2.3

Table 3 Results of the determination of CFA in tablets.

Sample	Content (mg)	Found (mg)	Recovery%	RSD%
Caffeic acid tablets	300	292.5 ± 8.19	97.5	2.8

Mean ± standard deviation (n = 5).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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