Determination of ascorbic acid by a modified multiwall carbon nanotube paste electrode using cetrimonium iodide/iodine

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A new modified graphite-multiwall carbon nanotube paste electrode for the determination of ascorbic acid (AA) based on cetrimonium iodide-iodine is described. The electrochemical response characteristics of the modified electrode toward AA were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in phosphate buffer solution (pH 2.0). When compared to activated carbon, graphite, and multiwall carbon nanotube paste electrode containing new modifier, the proposed modified paste electrode not only shifted the oxidation potential of AA towards less positive potential but also enhanced its oxidation peak current. Further, the oxidation of AA was highly stable at the modified paste electrode. The optimum analytical conditions were sought. The current response of AA increases linearly while increasing its concentration from 5.6×10^{-5} to 1.2×10^{-2} M with the correlation coefficient of 0.999 and a detection limit (3σ) was found to be 1.2×10^{-6} M. The present modified paste electrode was also successfully used for the determination of AA in the presence of common interference compounds. The present modified electrode was successfully used in the determination of AA in pharmaceutical and food samples.

Key Words: Cetrimonium iodide, iodine, multiwall carbon nanotube paste electrode, ascorbic acid

Introduction

L-Ascorbic acid (AA) is one of the most important cellular antioxidants and a valuable biomarker of oxidative stress. It has been found that AA can inhibit viral infectivity by inactivating viruses and by affecting

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viral replication. At the cellular level, AA can mitigate the reactive oxygen species production triggered by lipopolysaccharide and thereby prevents the induction of nitric oxide syntheses and excessive production of nitric oxide, which worsens oxidative stress in hepatocytes. Moreover, AA acts through redox-sensitive signaling pathways to induce tolerance in the dendritic cells of the immune system.[1] It can be synthesized by plants and by many mammals, but not by humans, and it is present in small quantities in food and is indispensable for life, health, and physical and daily activity.[2] In addition, ascorbate is important for neuronal maturation and function, as well as for protection of the brain against oxidant stress; this is well supported by the evidence presented in articles.[3] Therefore, the determination of AA has attracted much attention from researchers. A variety of methods and strategies have been reported for the determination of this analyte including voltammetry,[4−6] flow injection (FI) analysis,[7−9] spectrophotometry,[10,11] and chromatography.[12,13]

AA can be measured using voltammetry methods in order to gain the advantages of high sensitivity and selectivity. A carbon electrode, when subjected to an appropriate pretreatment procedure, exhibits a minimal propensity for surface fouling. However, the kinetics of electron transfer is quite sluggish. This last characteristic of electrochemical irreversibility means that AA can be oxidized only at potentials considerably removed from its standard redox potential. Therefore, some chemically modified electrodes with various active mediators immobilized at the electrode surface for the mediated oxidation of AA have been used.[14−16] In most cases the electrode substrates were GC, Pt, Au, and graphite. However, some authors have emphasized the instability of the attached or adsorbed materials on the electrodes as a problem arising in the utilization of chemically modified electrodes.[16,17] It seems that the incorporation of electrocatalysts into the electrode matrix can, even partly, help to solve this problem, and carbon paste electrodes spiked with catalyst may be suitable for this purpose.

Nanotubes, the last focus of scientists in a series of "all carbon" materials discovered over the last several decades, are the most interesting and have the greatest potential.[18] A huge, cylindrical surface area and graphene sheet CNT have special properties, such as high electrical conductivity, chemical stability, and catalyst support, which are useful for an analytical biosensor.[19] The CNT-modified electrodes promote electron transfer due to their conductivity and mechanical properties.[20] Several authors have reported the excellent electrocatalytic properties of nanotubes in the redox behavior of different biomolecules[21] The properties of carbon nanotubes paste electrode (CNTPE) based on the dispersion of carbon nanotubes within mineral oil have been demonstrated[2]

Iodine has been used extensively to flow injection determination of numerous organic compounds such as AA,[22] adrenaline,[23] cortisol,[24] and the highly carcinogenic aflatoxins.[25]

Various modifiers have been investigated intensively for modification of carbon paste electrodes (CPEs) for determination of AA.[26−29] To the best of our knowledge, no modified electrode such as CPE using cetrimonium iodide-iodine has been reported in the determination of AA. Farsang studied the redox behavior of the I_2/I^- system using a CPE made with silicone oil.[30] In his report, the redox system, I_2/I^-, was chemically reversible, but electrochemically irreversible, and the slow rate of polarization for the electrogenerated iodine species was attributed to its solubilization into the pasting liquid. Svancara and Konvalina demonstrated the synergistic effect of ion-pairing formation on the extractive preconcentration of iodide as iodine onto a carbon paste surface by using tricresyl phosphate as a pasting liquid.[31]

The cetrimonium cation or cetyltrimethylammonium ion (CTA^+) is a cationic surfactant and an effective

antiseptic agent against bacteria and fungi.[32] The closely related compounds cetrimonium bromide, cetrimonium chloride, and cetrimonium stearate are also used as topic antiseptics, and may be found in many household products such as shampoos and cosmetics. As a long-chain tetraalkylammonium salt, cetrimonium ion can be strongly adsorbed onto a CPE and forms an ion-pair compound with some anions, such as I^- and I_3^-. Therefore, it is a very good casting agent. This reagent as ion-pair with I^- and I_3^- with high molecular weight, 411.45 and 665.25 g mol^{-1} for $CTA^+ \cdot I^-$ and $CTA^+ \cdot I_3^-$ are stable under normal temperatures and pressures and slightly soluble in aqueous solution. Therefore, the accumulation of iodide as iodine is very effective, and significantly increases the sensitivity of the analysis.[33]

Insoluble cationic single-chain surfactant can form a stable monolayer on the CPE surface based on the hydrophobic interactions between the hydrophobic long chain of the cetyltrimethylammonium iodide (CTAI) molecule (Figure 1) and the paraffin oil in the carbon paste. This effect is often explained by a "synergistic adsorption" mechanism.[34] We used CTA^+ as insoluble cationic single chain surfactant for determination of AA. The present work describes for the first time the details of the development of a cetyltrimethylammonium iodide-iodine redox system as a new modifier in various paste electrodes such as activated carbon, graphite, multiwall carbon nanotube, and a mixture of graphite-multiwall carbon nanotube for electrocatalytic oxidation of AA. The practical application of the modified CPE was demonstrated by measuring the concentration of AA in real samples.
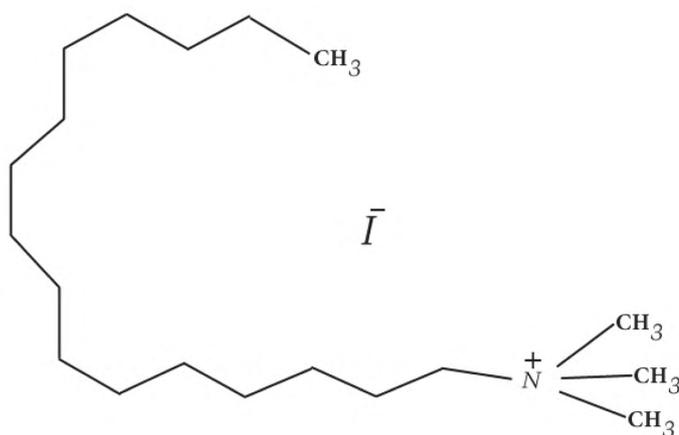
Figure 1. Chemical structure of cetyltrimethylammonium iodide.

Experimental

Reagents and materials

The AA was purchased from Fluka-Sigma and was used as received. Iodine (I_2), activated carbon (AC), graphite fine powder (G), and paraffin oil were obtained from Merck. Multiwall carbon nanotubes (MWCNTs) with nanotube diameters OD = 20-30 nm, wall thickness = 1-2 nm, length = 0.5-2 μm, and purity of >95%, and cetyltrimethylammonium bromide (CTAB) were purchased from Aldrich. Other chemical compounds such as H_3PO_4, NaH_2PO_4, and NaOH were purchased from Merck. Phosphate buffer solutions (PBSs) were prepared

from H_3PO_4 and NaH_2PO_4 (0.1 mol L^{-1}) and adjusted to pH range 2-10 with 0.1 mol L^{-1} H_3PO_4 and NaOH solutions and used as supporting electrolyte. All solutions were prepared using doubly distilled water (DDW). The electrolyte solutions were deoxygenated with nitrogen bubbling before each voltammetric experiment. All experiments were performed under nitrogen atmosphere at room temperature. All solutions were freshly prepared with DDW and all other chemicals used were of analytical reagent grade. The cetyltrimethylammonium iodide (CTAI) was prepared as described by Cerritelli et al. as follows.[35] Potassium iodide was added to a solution of CTABr (1 g) in DDW (50 mL). The precipitate was recovered by filtration and purified by recrystallization from acetone to yield CTAI as a white solid (1.1 g, 95% yield). The residual was dried in vacuum at 50 °C for 24 h to give $(C_{16}H_{33})N^+(CH_3)_3$. I^- ion-pair.

Instrumentation

All electrochemical experiments were carried out in a conventional 3-electrode cell at room temperature. Electrochemical measurements were made with a SAMA500 Electroanalyzer (SAMA Research Center, Iran) controlled by a personal computer. A platinum electrode and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. A Metrohm 632 pH-meter with a Metrohm double junction glass electrode was used for monitoring pH adjustment.

Preparation of working electrodes

A mixture of 1.1 % (W/W) CTAI and 1.6 % (w/w) I_2 spiked AC or G or MWCNT or G-MWCNT was made by dissolving the given quantity of CTAI and I_2 in ethanol and hand mixing with 99 times its weight of AC or G or MWCNT or a mixture of G-MWCNT (3:1) with a mortar and pestle. The solvent was evaporated by stirring. A mixture 2:1 from the above resulting mixture and paraffin was blended by hand-mixing and the resulting paste was then inserted in the bottom of a polypropylene tube. The electrical connection was implemented by a copper wire lead fitted into the polypropylene tube. The electrodes were denoted as ACPE/CTAI-I_2, G PE/CTAI-I_2, MWCNTPE/CTAI-I_2, and G-MWCNTPE/CTAI-I_2. Furthermore, the CPE with 1.1% (W/W) CTAI or 1.6% (w/w) I_2 was prepared with same method. A CPE without CTAI-I_2 was used as a blank to determine the background current. When not in use, the modified electrode was stored in DDW.

Results and discussion

The electrochemical study of different PEs

The electrochemical behavior of CTAI, I_2, and CTAI-I_2 couple was studied at the surface of different CPEs with AC by cyclic voltammetry over a potential range from –0.1 to 1 V. Figure 2 shows the cyclic voltammograms of 3 CPEs containing CTAI (ACPE/CTAI), I_2 (ACPE/I_2), and CTAI-I_2 (ACPE/CTAI-I_2), respectively. As shown in Figure 2a, curve 1, there are no anodic and cathodic peaks for ACPE/CTAI. Figure 2b (curves 1-5) shows the cyclic voltammograms of ACPE/I_2 in consecutive 5 potential scan cycles; such results could prove the instability of the modified electrode. Figure 2a, curves 2-6, shows cyclic voltammograms of ACPE/THAI-I_2 in 5 consecutive potential-scan cycles. As shown in Figure 2a, curves 2-6, a slight change in the anodic peak currents was observed ($\Delta I = 1.2$ μA); such results could prove the stability of the modified electrode. On the

other hand, there is a slight change in the anodic peak potential observed after the 5 consecutive potential-scan cycles from 0.517 to 0.522 V; then the anodic peak potential is constant at about 0.522 V, corresponding to the oxidation of iodide to iodine; at a reversal scan no reduction peak was observed. Based on a Farsang report,[31] the redox system, I_2/I^-, was chemically reversible, but electrochemically irreversible, and the slow rate of polarization for the electrogenerated iodine species was attributed to solubilization into a pasting liquid, such as silicone oil. Moreover, when CTAI was added, we presumed that both iodide ions (I^-) and iodine (I_3^-) may partly form ion-pairs with cetyltrimethylammonium cations (CTA^+), and are adsorbed on the electrode surface because of the strong affinity of lipophilic carbon paste for $CTA^+.I^-$ and $CTA^+.I_3^-$ ion-pairs. By comparisons of Figures 2a and 2b, the affinity of I_3^- towards THA^+ may be much stronger than I^- towards it.
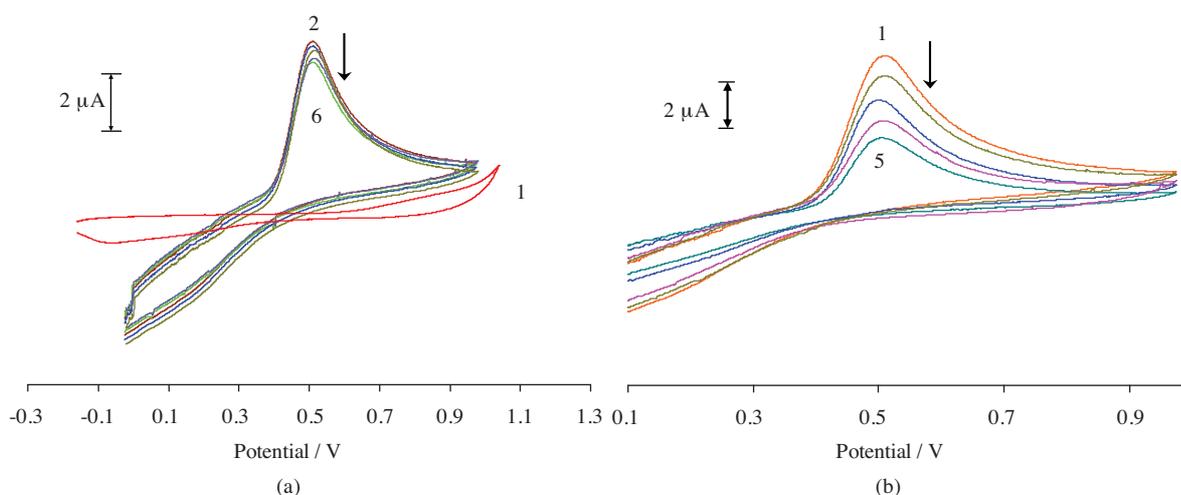
Figure 2. Cyclic voltammograms of modified paste electrodes (a) ACPE/CTAI (curve 1) and ACPE/CTAI-I_2 in 5 consecutive potential scan cycles (curves 2-6). (b) ACPE/I_2 in 5 consecutive potential scan cycles. Conditions: pH 2 of PBS 0.1 M at 50 mV s^{-1}.

The effect of pH on the ACPE /CTAI-I_2 signal was investigated by differential pulse voltammetry (Figure 3a). The variations of anodic peak potential and anodic peak current with respect to the change in the pH of the electrolyte in the pH range from 2.0 to 10.0 were shown in Figure 3b. In addition, by increasing the pH of the buffer solution from 2.0 to 10.0, a negative shift is observed in the I^-/I_3^- redox peak potential, which showed that this I^-/I_3^- redox underwent a proton-electron process.

Figure 4 shows the cyclic voltammograms and differential pulse voltammograms over a potential range from –0.1 V to 1.1 V, which is related to ACPE, ACPE /CTAI-I_2, GPE/CTAI-I_2, and G-MWCNTPE/CTAI-I_2. As shown in Figure 4a, in a positive scan, an oxidation peak was obtained at about 0.47 V for GPE/CTAI-I_2, corresponding to the oxidation of iodide to iodine (I^-/I_3^-). Moreover, at a reversal scan no reduction peak of iodine to iodide (I_3^-/I^-) was observed. In the same condition, an oxidation peak was obtained at about 0.44 V for G-MWCNTPE/CTAI-I_2, corresponding to the oxidation of iodide to iodine (I^-/I_3^-), and, at a reversal scan, a reduction peak of iodine that formed in the previous scan occurred at nearly 0.24 V. A summary of electrochemical data for the CPEs is shown in Table 1. Based on cyclic voltammogram for

G-MWCNTPE/CTAI-I_2, the potential of the anodic (E_{pa}) and cathodic (E_{pc}) peaks and half-wave potential ($E_{1/2}$) are 0.44 V, 0.24 V, and 0.34 V, respectively. Furthermore, the peak separation potential, ΔE_p ($\Delta E_p = E_{pa} - E_{pc} = 0.20$ V), is greater than the $0.059/n$ V expected for a reversible system; this result suggests that I^-/I_3^- couple does not act as a reversible system in the G-MWCNTPE/I_2-CTAI matrix indicating the quasi-reversible monoelectronic charge-transfer process of I^-/I_3^- couple at the paraffin oil-based CPEs. The corresponding reactions of these voltammograms are as follows:

$$3I^- \rightleftharpoons I_3^- + 2e^-. \tag{1}$$

Equation (1) includes the oxidation of iodide ion (I^-) and reduction of iodine ion (I_3^-) with loss of 2 electrons in the anodic sweep.
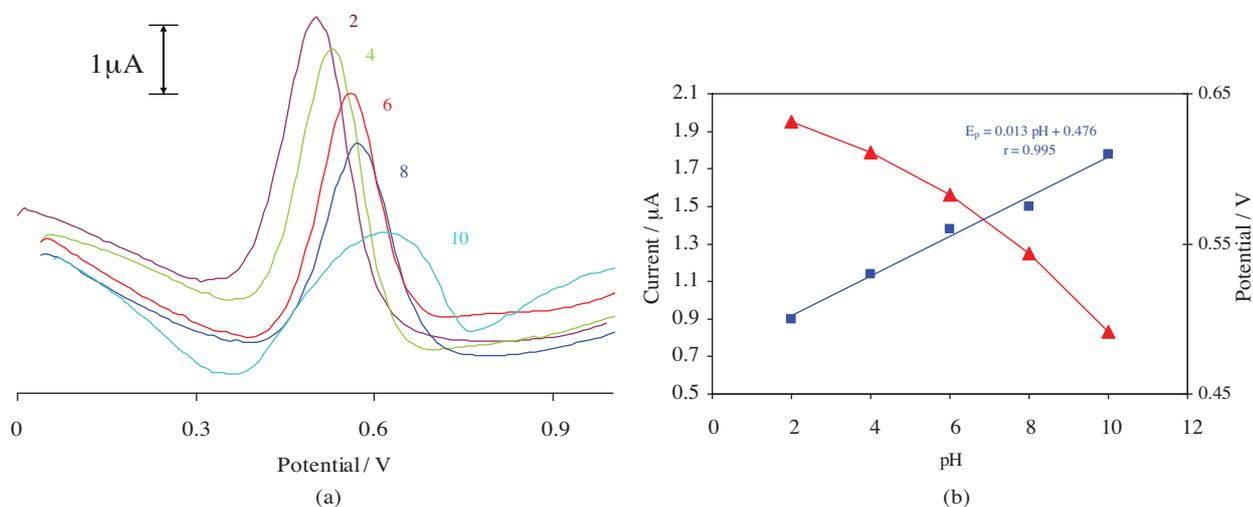
Figure 3. (a) Differential pulse voltammograms of ACPE/TAI-I_2 at various pH values 2.0, 4.0, 6.0, 8.0, and 10.0. (b) The effect of pH on the anodic peak current and anodic peak potential of ACPE/I_2-CTAI.

Table 1. Electrochemical data for different PEs (vs. SCE)[a].

Electrode type	E_{pa}/mV	E_{pc}/mV	$E_{1/2}$/mV	ΔE_p/mV	System type
ACPE/CTAI-I_2^b	0.512	-	-	-	irreversible
GPE/CTAI-I_2^b	0.470	-	-	-	irreversible
G-MWCNTPE/CTAI-I_2^c	0.442	0.264	0.352	0.178	quasi-reversible

[a] Scan rate = 50 mV s^{-1} and pH 2.0 of PBS (0.1 M).

[b] CTAI = 1.1% (W/W) and I_2 = 1.6% (w/w).

[c] G:MWCNT; 3:1, CTAI = 1.1% (W/W) and I_2 = 1.6% (w/w).
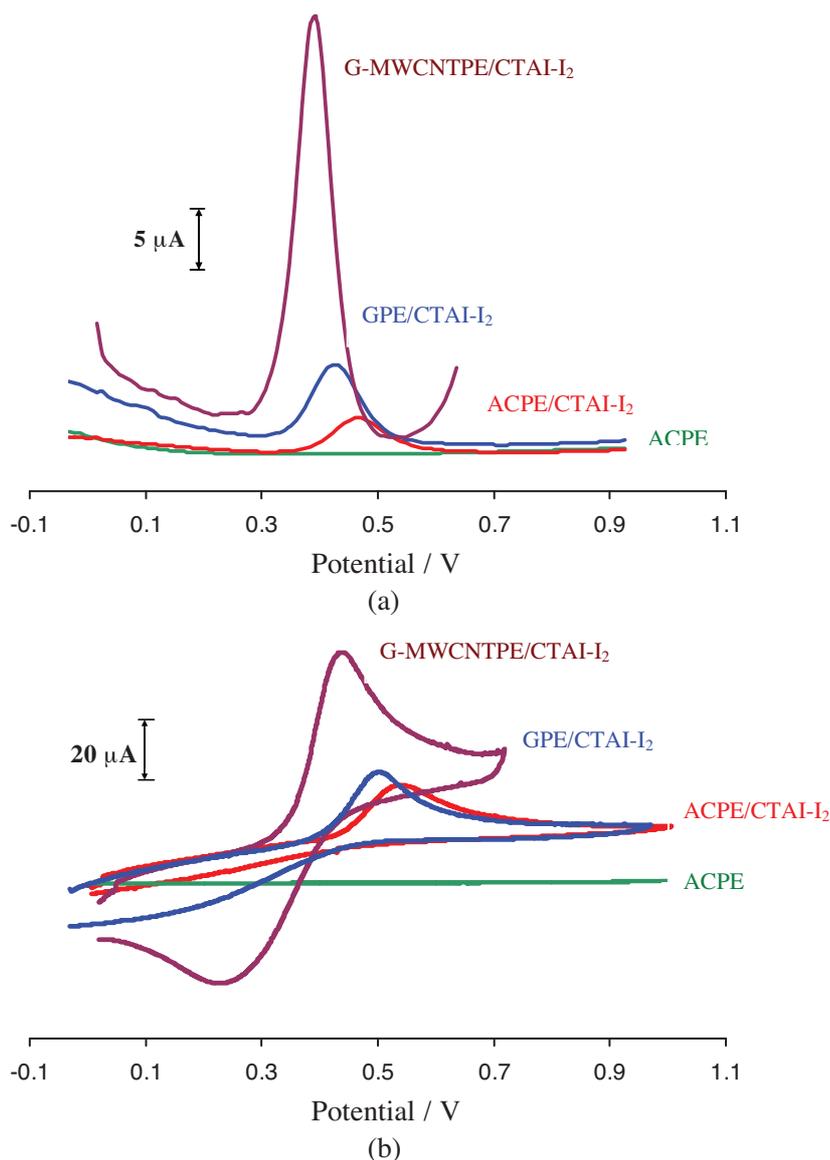
Figure 4. (a) Cyclic voltammograms and (b) differential pulse voltammograms of ACPE, ACPE/CTAI-I_2, GPE/CTAI-I_2, and G-MWCNTPE/CTAI-I_2 in PBS with pH 2 at scan rate 50 mV s^{-1} (GCPE and G-MWCNTPE are the same as ACPE and are not shown in figure).

The scan rate dependence of the modified electrode was studied. In Figure 5, the cyclic voltammograms of the G-MWCNTPE/CTAI-I_2 electrode in the selected range at various scan rates are shown. Plots of the peak currents versus the scan rate for both the anodic and cathodic peaks (Figure 5b) are linear for sweep rates of 25-750 mV s^{-1}. As shown in Figure 5b, I_{pa} and I_{pc} were linearly dependent on the scan rate, as expected for a surface confined redox process. These behaviors are consistent with a diffusionless system and reversible electron transfer process at low scan rates.[36] The values of the cathodic and anodic peak potential shift slightly toward the negative and positive directions, respectively, with increasing scan rate from 150 to 750.
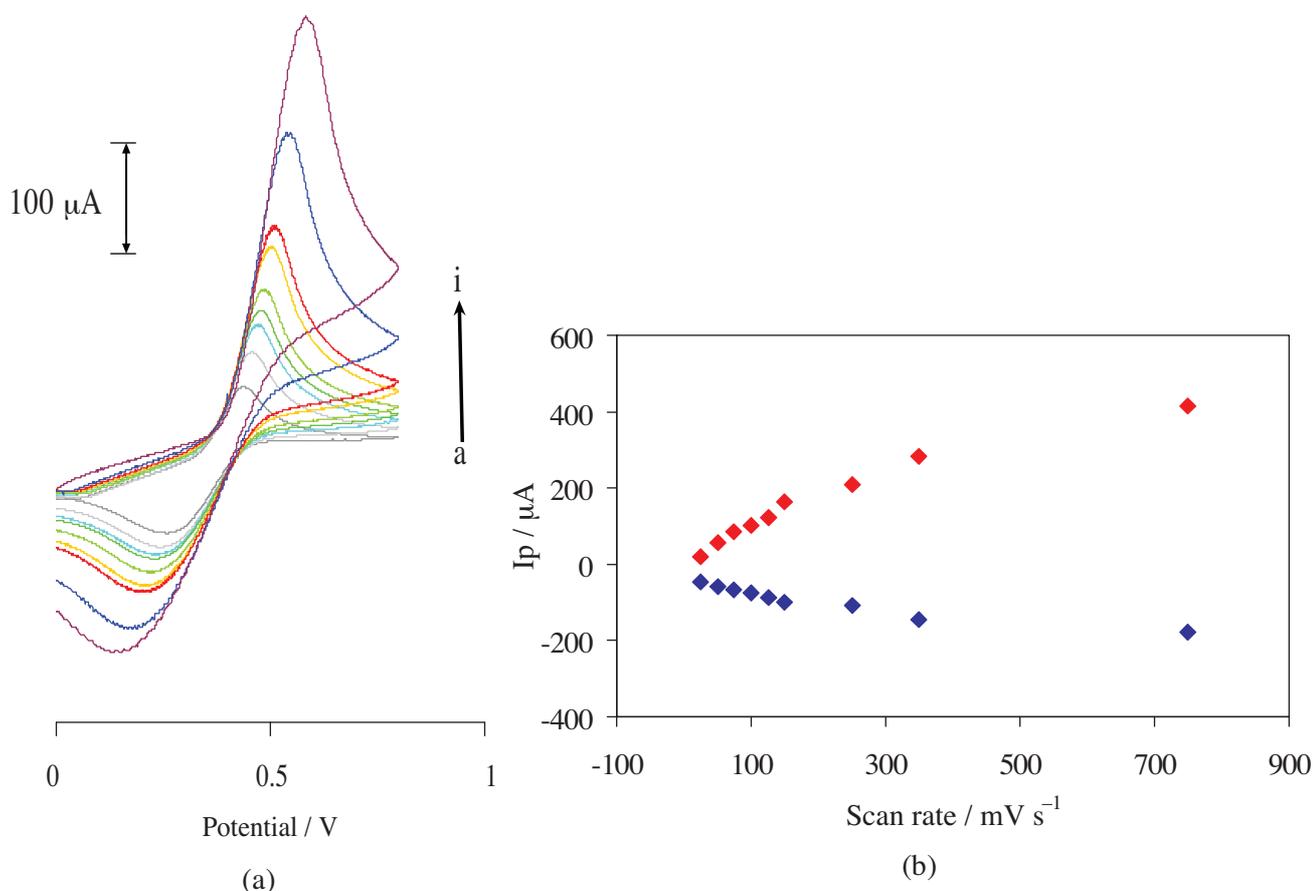
Figure 5. Cyclic voltammograms of G-MWCNTPE/CTAI-I_2 in 0.1 M PBS with pH 2, at various scan rates: (a) 25; (b) 50; (c)75; (d) 100; (e) 125; (f) 150; (g) 250; (h) 350; (i) 750 mV s^{-1}; (b) Plots of anodic and cathodic peak currents of G-MWCNTPE/CTAI-I_2 vs. scan rate.

The stability of G-MWCNTPE/CTAI-I_2 was studied by noting the decrease in anodic charge, q_a, in repetitive potential scan cycles. The rate of loss of electrochemical activity for the modified electrode was investigated prior to use. Cyclic voltammograms of G-MWCNTPE/CTAI-I_2 were obtained in consecutive 5 potential scan cycles in PBS at a scan rate of 50 mV s^{-1} (Figure 6). Only a small change in anodic and cathodic peak currents was observed and these results could prove the stability of the modified electrode.

Electrocatalytic oxidation of AA at the surface of different PEs

The prime objective of the present work was to determine the concentration of AA using modified CPEs. Figure 7 shows the CVs obtained for different modified CPEs in 0.1 M PBS pH 2.0 containing 0.5 mM AA. The ACPE, ACPE/CTAI-I_2, GPE/CTAI-I_2, and G-MWCNTPE/CTAI-I_2 electrodes showed an oxidation wave for AA at 660 mV, 536 mV, 496 mV, and 465 mV and a current difference ($\Delta I/\mu A$) for 5.5 μA, 3.5 μA, 8.6 μA, and 18.6 μA, respectively. On the other hand, when the G-MWCNTPE/CTAI-I_2 electrode was compared to

ACPE, ACPE/CTAI-I_2, and GPE/CTAI-I_2 electrodes, the oxidation peak potential of AA was shifted to 195 mV, 164 mV, and 124 mV less positive potential. It is shown that the cyclic voltammogram of the oxidation peak potential of AA acid at the modified CPEs shifted to the negative direction compared with unmodified CPEs, and the peak current at the modified CPEs also increased. The results indicate that the electrocatalytic activity of the modified electrode can be applied to the determination of AA. Moreover, the oxidation current for the G-MWCNTPE/CTAI-I_2 electrode was greatly increased in comparison of ACPE, ACPE/CTAI-I_2, and GPE/CTAI-I_2. The mechanism of this phenomenon can be written as follows:

$$3I^- \rightarrow I_3^- + 2e^-, \tag{2}$$

$$I_3^- + AA \rightarrow 3I^- + DHAA + 2H^+, \tag{3}$$
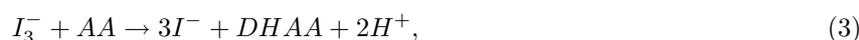
These results showed that the electrooxidation of AA to dehydroascorbic acid (DHAA) can be catalyzed by I^-/I_3^- couple as a mediator at the surface of the modified electrode.
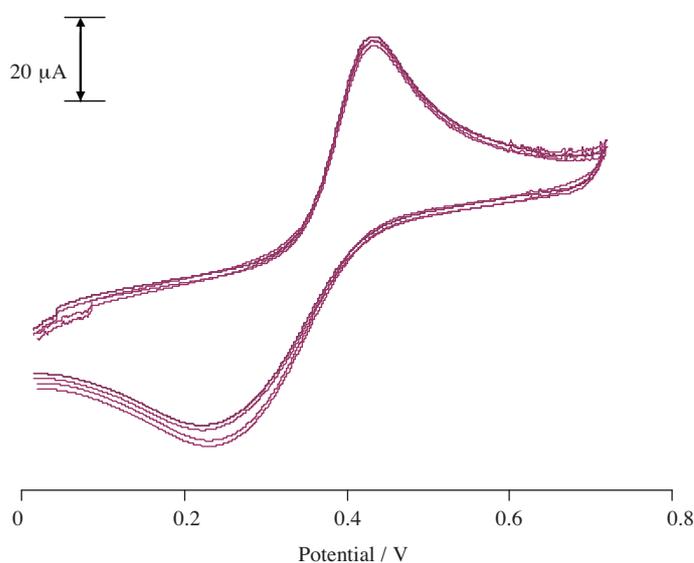
Figure 6. Cyclic voltammograms of G-MWCNTPE/CTAI-I_2 in 5 consecutive potential scan cycles in PBS (pH 2.0) at a scan rate of 50 mV s^{-1}.

In order to obtain the best composition of the G-MWCNTPE/CTAI-I_2 electrode, we used different quantities ratio of G:MWCNT, 1:3, 2:2, 3:1, 3.5:0.5, to prepare modified electrodes. For this work, with increases in the MWCNT amount (G:MWCNT; 1:3, 2:2), the anodic peak potential for the G-MWCNTPE/CTAI-I_2 electrode was shifted to positive potential, and with decreases in the MWCNT amount (G:MWCNT; 3.5:0.5), the anodic peak potential for the G-MWCNTPE/CTAI-I_2 electrode was similar to that of the GPE/CTAI-I_2 electrode. Based on these results, we selected the optimum composition 3:1 (G:MWCNT) in all experimental works.
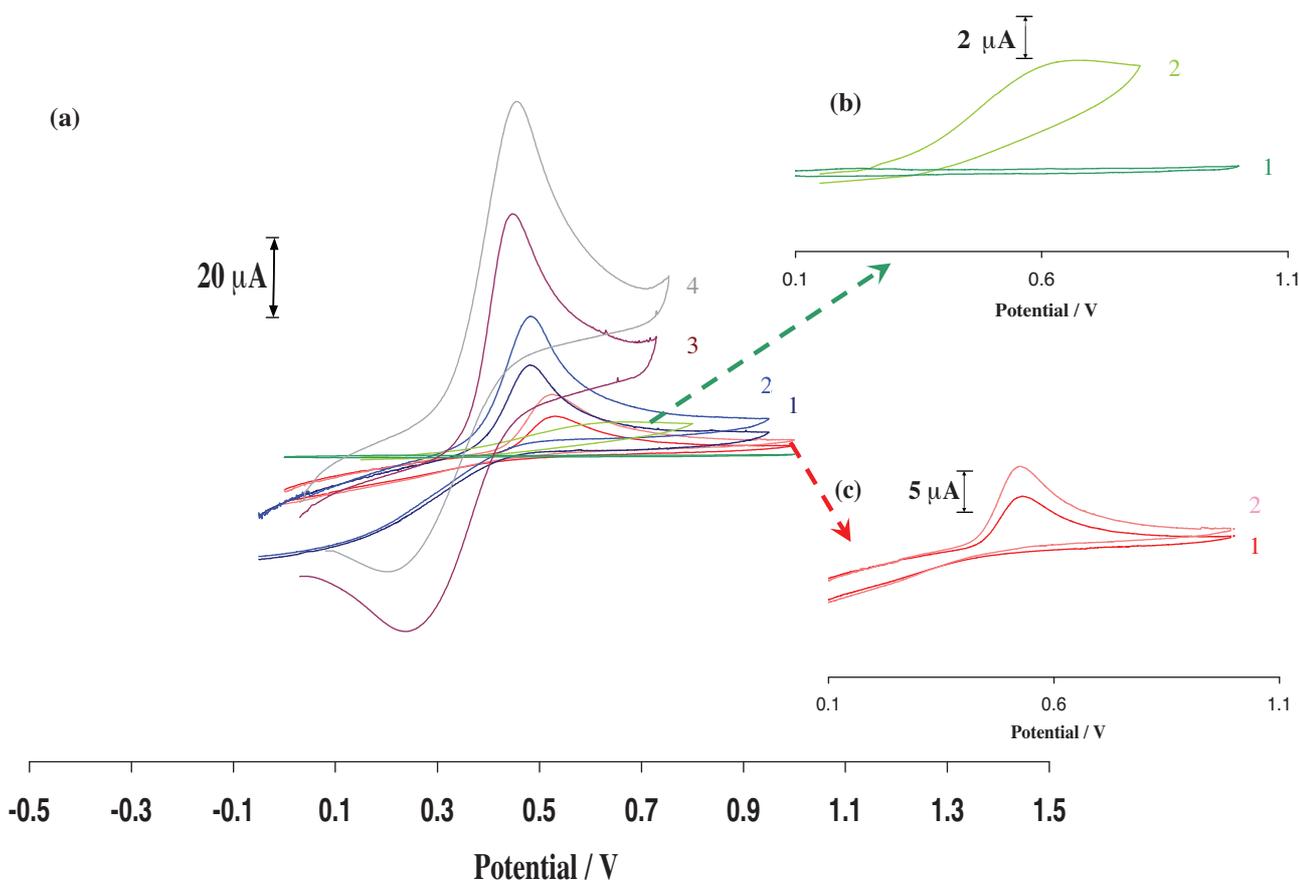
Figure 7. (a) Cyclic voltammograms of different modified CPE for determination of AA. GPE/CTAI-I$_2$ in absence of AA (a1) and in present of AA (a2) and G-MWCNT/CTAI-I$_2$PE in absence of AA (a3) and in presence of AA (a4). (b) ACPE in absence of AA (b1) and in presence of AA (b2). (c) ACPE /CTAI-I$_2$ and in absence of AA (c1) in presence of AA (c2). Conditions: in PBS with pH 2.0 at scan rate 50 mV s^{-1} and [AA] = 6.9 $\times$ 10^{-4} M AA for curves a2, a4, b2, and c2.

Evaluation of the proposed modified electrode

Under optimum conditions, determination of AA was carried out at the potential range of 0.1 to 1.0 V using differential pulse voltammetry mode. The AA electrooxidation peak was observed at the potential of about 0.442 V versus SCE. The electrocatalytic peak current of AA at the surface of G-MWCNT/CTAI-I$_2$PE was linearly dependent on the AA concentration. These peak currents were linear up to 0.012 M and were described by the equation $\Delta I_{(\mu A)} = 3322.5 \, [AA] + 4.7$, r = 0.9991, n = 10, where $\Delta I_{(\mu A)}$ is the difference of the oxidation peak currents of G-MWCNTPE/CTAI-I$_2$ before and after addition of AA, $[AA]_{(M)}$ is the AA concentration, r is the correlation coefficient, and n represents the number of determinations (Figure 8). The detection limit (DL) was calculated using the equation DL = $3 S_{bk}/m$, where S_{bk} is the standard deviation of blank signals for 10 determinations (1.3 $\times$ 10^{-3}) and m is the slope of the calibration graph (3322.5). The calculated DL

was found to be 1.2×10^{-6} M. Relative standard deviation (RSD %) for 5 determinations of AA with 4.6×10^{-4} M concentration was 0.6%.
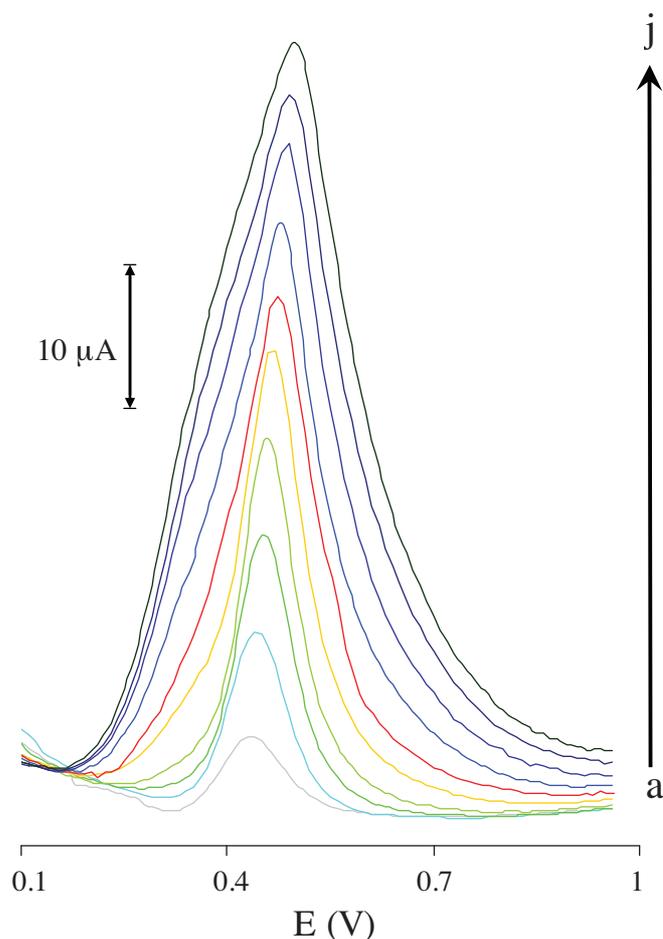
Figure 8. (a) Differential pulse voltammograms of AA at various concentration (from a to m): 0.0, 5.6×10^{-5}, 9.5×10^{-4}, 2.3×10^{-3}, 3.7×10^{-3}, 5.3×10^{-3}, 6.4×10^{-3}, 7.8×10^{-3}, 9.9×10^{-3}, 1.0×10^{-2}, and 1.2×10^{-2} M at surface of the G-MWPE/CTAI-I_2.

Interference study

The influence of other several compounds such as lactose, maleic acid, glycine, maltose, saccharose, fructose, oxalic acid, succinic acid, tartaric acid, and glucose on the electrocatalytic peak current of AA oxidation at the surface of G-MWCNTPE/CTAI-I_2 was examined using cyclic voltammetry. The tolerance limit was taken as the maximum concentration of the foreign substances that caused an approximately 5% relative error for 1.2×10^{-4} mol L^{-1} AA. The experimental results showed that the presence of these compounds (except glucose) did not significantly influence the determination of AA under the experimental conditions. Therefore, this result demonstrated the selectivity of this method for the voltammetric determination of AA. The results are listed in Table 2.

Table 2. Effect of diverse substances on the analysis of 1.2×10^{-4} mol L^{-1} AA. Conditions: G:MWCNT = 3:1, CTAI = 1.1% (W/W) and I$_2$ = 1.6% (w/w), scan rate = 50 mV s^{-1}, and pH 2.0 of PBS (0.1 M).

Substance	[Interference substance]/[AA]
Maleic acid, glycine, maltose	1000
Saccharose, lactose	500
Tartaric acid, fructose	100
Succinic acid, oxalic acid	50
Glucose	10

Application in real samples

In order to demonstrate the catalytic oxidation of AA in the real sample, we examined this ability in the voltammetric determination of AA in some pharmaceutical preparations and foods. Orange juice and pharmaceutical samples such as AA tablets and powder (purchased from local sources) were selected as real samples for analysis by the proposed method using the standard addition method in order to prevent any matrix effect. The results were compared with those obtained using the official iodometric titration method.[37] The paired t-test equation, applied in statistics, is

$$t = \left| \frac{\overline{d}\sqrt{n}}{s_d} \right| \tag{4}$$

where $\overline{d}$ and s$_d$ are the mean and standard deviation respectively of $\overline{d}$ (the difference between paired values). For the pairs of values in Table 3, the mean difference, $\overline{d}$, is –2.275 and the standard deviation of the differences, s$_d$, is 3.17. The calculated $|t|$ was found to be 1.44. The critical value of t (tabulated t) for n – 1 degrees of freedom (in this work 3) is 3.18 (P = 0.05). Since the calculated value of t is less than this the null hypothesis is not rejected: the methods do not give significantly different results for AA concentration.[38]

Table 3. Determination of AA in real samples with using G-MWPE/CTAI-I$_2$ electrode. Conditions: G:MWCNT = 3:1, CTAI = 1.1% (W/W) and I$_2$ =1.6% (w/w), scan rate = 50 mV s^{-1}, and pH 2.0 of PBS (0.1 M).

Sample	Claimed preparation/mg	Proposed method[a]/mg (±SD)	Iodine method[a]/mg (±SD)	Recovery (%)
AA tablet	250 per tablet	239.3(±1.4)	243.6(±1.9)	98.2
AA powder	500 per sachet	481.5(±1.6)	485.2(±1.2)	99.2
Baluchestani lemon (100 mL)	—	58.6(±2.1)	59.9(±2.5)	97.8
Egyptian orange (100 mL)	—	88.1(±2.1)	84.8(±2.3)	103.9

[a.] Results based on 5 replicate determinations per sample.

Conclusions

The construction of a graphite-multiwall carbon nanotube/cetyltrimethylammonium iodide-iodine paste electrode and its use for electrocatalytic oxidation and determination of different concentrations of AA was described. The overpotential was reduced with the value of 195 mV for the oxidation of AA. Experimental conditions such as pH 2 of supporting electrolyte, scan rate 50 mV s^{-1}, and composition of the G-MWCNTPE/I$_2$-CTAI were used for the determination of AA. For studying the capability of this modified electrode in real samples, some pharmaceutical preparations and foods were used and compared with the standard titrimetric method. There was no significant difference between the 2 methods. Its simple fabrication procedure, wide linear range, high stability, and good reproducibility for repeated determination suggest that this electrode is a good, cheap, and attractive candidate for practical applications.

Acknowledgment

References

1. Sun, X.; Niu, Y.; Bi, S.; Zhang, S. *J. Chromatogr. B* **2008**, *870*, 46-50.

2. Garrido Frenich, A.; Hernández Torres, M. E.; Belmonte Vega, A.; Martínez Vidal, J. L.; Plaza Bolanos, P. *J. Agric. Food Chem.* **2005**, *53*, 7371-7376.

3. Harrison, F. E.; May, J. M. *Free Radical Biology & Medicine* **2009**, *46*, 719-730.

4. Khorasani-Motlagh, M.; Noroozifar, M. *Turk. J. Chem.* **2004**, *28*, 369-378.

5. Dursun, Z.; Pelit, L.; Taniguchi, I. *Turk. J. Chem.* **2009**, *33*, 223-231.

6. Sahin, M.; Ozcan, L.; Usta, B.; Sahin, Y. *Biosens. Bioelectron.*, **2009**, *24*, 3492 -3497.

7. Gilbert, O.; Kumara Swamy, B. E.; Chandra, U.; Sherigara, B. S. *J. Electroanal. Chem.* **2009**, *636*, 80-85.

8. Noroozifar, M.; Khorasani-Motlagh, M. Akhavan, K.; *Anal. Sci.* **2005**, *21*, 655-659.

9. Noroozifar, M.; Khorasani-Motlagh M.; Farahmand, A. R. *Acta. Chim. Slov.* **2004**, *51*, 717-727.

10. Takayanagi, T.; Nishiuchi, M.; Ousaka, M.; Oshima, M.; Motomizu, S. *Talanta*, **2009**, *79*, 1055-1060.

11. Noroozifar, M.; Khorasani-Motlagh, M. *Turk. J. Chem.* **2003**, *27*, 717-722.

12. Burini, G. *J. Chromatogra. A* **2007**, *1154*, 97-102.

13. Li, X.; Franke, A. *J. Chromatogr. B* **2009**, *877*, 853-856.

14. Miller, L. L.; Kitani, A. *J. Am. Chem. Soc.* **1981**, *103*, 3595-3597.

15. Angnes, L.; Matos R. C.; Augelli, M. A.; Lago, C. L. *Anal. Chim. Acta*, 2000, *404*, 151-157.

16. Kuwana, T.; Ueda, C.; Tse, D. C. S. *Anal. Chem.* **1982**, *54*, 850-856.

17. Raoof, J. B.; Ojani, R.; Hosseinzadeh, R.; Ghasemi, V. *Anal. Sci.* **2003**, *19*, 1251-1258.

18. Marinkovi, S. N. *J. Serb. Chem. Soc.* **2008**, *73*, 891-913.

19. Young Ly, S. *Bioelectrochemistry* **2006**, *68*, 227-231.

20. Anık, Ü.; Çubukçu, M. *Turk. J. Chem.* **2008**, *32*, 711-719.

21. Rubianes, M. D.; Rivas, G. A. *Electrochem. Commun* **2003**, *5*, 689-694.

22. Noroozifar, M.; Khorasani-Motlagh, M. *Talanta* **2003**, *61*, 173-179

23. Kojo, A; Martínez, C. J. *Anal. Chim. Acta* **1995**, *308*, 334-339.

24. Carlton, M.; Hasler, M.; Painter, K. *Radiochem. Radioanal. Lett.* **1979**, *39*, 19-25.

25. Jansen, H; Jansen, R.; Brinkman, U. A.; Frei, R. *Chromatographia* **1987**, *24*, 555-561.

26. Raoof, J. B.; Ojani, R.; Rashid-Nadimi, S. *Electrochim. Acta* **2004**, *49*, 271-280.

27. Akbari, R.; Noroozifar, M.; Khorasani-Motlagh, M; Taheri, A. *Anal. Sci.* **2010**, *26*, 425-430.

28. Nalini, B.; Narayanan, S. S. *Anal. Chim. Acta* **2000**, *405*, 93-97.

29. Guorong, Z.; Xiaolei, W.; Xingwang, S.; Tianling, S. *Talanta* **2000**, *51,* 1019-1025.

30. Farsang, G. *Acta Chim. Hung.* **1965**, *45*, 163-169.

31. Svancara, I. ; Konvalina, J. *Electroanalysis* **1998**, *10*, 787-795.

32. Lundblad, R. L.; MacDonald, F. M. *Handbook of Biochemistry and Molecular Biology*, 4th ed., CRC Press, 2010, Chap. 88, pp. 813-818.

33. He, Q.; Fei, J.; Hu, S. *Anal. Sci.* **2003**, *19*, 681-686.

34. Xu, Y.; Hu, C.; Hu, S. *Bioelectrochemistry* **2009**, *74*, 254-259.

35. Cerritelli, S.; Chiarini, M.; Cerichelli, G.; Capone, M.; Marsili, M. *Eur. J. Org. Chem.* **2004**, 623-630.

36. Fernández, L.; Carrero, H. *Electrochim. Acta*, **2005**, *50*, 1233-1240.

37. Izuagie A. A.; Izuagie, F. O. *J. Agricul. Biol. Sci.* **2007**, *3*, 367-369.

38. Miller J. C.; Miller, J. N. *Statistics for Analytical Chemistry*, 2nd ed., John Wiley and Sons, New York, 1988.