Preparation of Tetraheptylammonium Iodide-Iodine Graphite-Multiwall Carbon Nanotube Paste Electrode: Electrocatalytic Determination of Ascorbic Acid in Pharmaceuticals and Foods

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The present work describes the construction of a new modified graphite-multiwall carbon nanotube paste electrode by casting the appropriate mixture of tetraheptylammonium iodide-iodine as a new modifier. The modified paste electrode was used for the determination of ascorbic acid (AA) in a phosphate buffer solution (pH 2.0). When compared to activated carbon, a graphite and multiwall carbon nanotube paste electrode containing a new modifier, the proposed modified paste electrode not only shifted the oxidation potential of AA towards a 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 a correlation coefficient of 0.9991; the detection limit (3σ) was found to be of 3.6×10^{-5} 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 demonstrated towards the determination of AA in pharmaceutical and food samples.

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Ascorbic acid (AA), a water-soluble compound, is an important micronutrient that, besides its antioxidant effect, is valuable for its vitamin action with playing many physiological roles. During recent years, interest in AA has also increased because of its involvement in the liberation of nitric oxide under various conditions. It can be synthesized by plants and by many mammals, but not by man; it is present in small quantities in food and is indispensable for life, health, and physical and daily activity.¹ In addition, ascorbate is important for neuronal maturation and function, as well as for protection of the brain against oxidant stress, is well supported by evidence presented in articles.² Therefore, the determination of AA has attracted much attention of researchers. In view of the great importance and wide use of AA, numerous analytical techniques have been proposed for its determination in different matrices and at different levels. These include voltammetry,³⁻⁵ flow injection (FI) analysis,⁶⁻⁸ spectrophotometry,^{9,10} and chromatography.¹¹⁻¹³ AA can be measured using voltammetry methods in order to gain the advantages of high sensitivity and selectivity. For this purpose, various chemically modified electrodes have been constructed.¹⁴⁻¹⁷

Carbon nanotubes (CNTs) combine in a unique way high electrical conductivity, high chemical stability and extremely high mechanical strength. These special properties of both single-wall (SW) and multi-wall (MW) CNTs have attracted the interest of many researchers in the field of electrochemical sensors.¹⁸ Several authors have reported excellent electrocatalytic

properties of nanotubes in the redox behavior of different biomolecules.¹⁹ The properties of a carbon nanotubes paste electrode (CNTPE) based on the dispersion of CNTs within mineral oil have been demonstrated.¹⁹

Iodine has been extensively used to flow-injection determinations of numerous organic compounds, such as AA,²⁰ adrenaline,²¹ cortisol²² and the highly carcinogenic aflatoxins.²³

Various modifiers have been intensively investigated for the modification of carbon paste electrodes (CPE) for the determination of AA.²⁴⁻²⁷ To the best of our knowledge, no modified electrode, such as CPE using iodine, has been reported concerning the determination of AA.

Farsang studied the redox behavior of the I_2/I^- system using a CPE made with silicone oil.²⁸ In the present work, 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 a 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.²⁹

The present investigation studied the determination of AA at CPEs using tetraheptylammonium iodide-iodine (THAI- I_2) as a new redox system. As a long-chain tetraalkylammonium salt, THAI can be strongly adsorbed onto a CPE and formed an ion-pair compound with some anions, such as I^- and I_3^- . This reagent with high molecular weight, $537.70 \text{ g mol}^{-1}$ is stable under normal temperatures and pressures and slightly soluble in aqueous solution. So, it is a very good casting agent. There is no any report for application of THAI (Fig. 1) for

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Fig. 1 Chemical structure of tetraheptylammonium iodide.

electroanalytical determinations in literature. THAI is safe and available as a commercial chemical compounds. This paper describes for the first time the details of the development of THAI/I₂ 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 PE was demonstrated by measuring the concentration of AA in some real and pharmaceutical samples.

Experimental

Reagents and materials

Tetraheptylammonium iodide (THAI), iodine (I₂), activated carbon (AC), graphite fine powder (G), paraffin oil and lithium sulfate (as supporting electrolyte) were obtained from Merck company. Ascorbic acid (AA) was purchased from Fluka-Sigma, and was used as received. Multiwall carbon nanotubes (MWCNT) with nanotube diameters (o.d., 20 – 30 nm; wall thickness, 1 – 2 nm; length, 0.5 – 2 μm) and purity of >95% was purchased from Aldrich. Other chemical compounds, such as H₃PO₄, NaH₂PO₄ and NaOH, were purchased from Merck. Phosphate buffer solutions (PBS) were prepared from H₃PO₄ and NaH₂PO₄ (0.1 mol L⁻¹), adjusted the pH range over 2.0 – 10.0 with 0.1 mol L⁻¹ H₃PO₄ and NaOH solutions, and were used as supporting electrolytes. All solutions were prepared using doubly distilled water (DDW). The electrolyte solutions were deoxygenated with a 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.

Instrumentation

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

Preparation of working electrodes

To eliminate metal and metal oxide catalysts within the nanotubes, a 0.2-g amount of MWCNT was dispersed in 60 ml of 4.0 M HCl for 4 h with the aid of ultrasonic agitation, rinsed thoroughly with distilled water to neutrality and finally dried. A 0.05-g amount of MWNT was dispersed in a 60-ml mixture of concentrated HNO₃ and H₂SO₄ (1:3 v/v) with the aid of ultrasonic agitation for 4 h in a water bath, then washed with distilled water to neutrality and dried.

A mixture of 1.0% (w/w) THAI and 1.7% (w/w) I₂ spiked AC or G or MWCNT or G-MWCNT was made by dissolving the given quantity of THAI and I₂ 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 2:1 mixture 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. Electrical connection was implemented by a copper wire lead fitted into the polypropylene tube. The electrodes are denoted as AC/THAI-I₂PE, G/THAI-I₂PE, MWCNT/THAI-I₂PE and G-MWCNT/THAI-I₂PE. Also, the CPE with 1.0% (w/w) THAI or 1.7% (w/w) I₂ was prepared by same method. A CPE without THAI-I₂ 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 a THAI, I₂ and THAI-I₂ couple was studied at the surface of different CPE with AC by cyclic voltammetry over a potential range from 0.1 to 1 V. Figures 2a and 2b show cyclic voltammograms of two CPEs which contain THAI (AC/THAIPE) and I₂ (AC/I₂PE), respectively. As shown in Fig. 2a, there are no anodic and cathodic peaks. Figure 2b shows cyclic voltammograms of AC/I₂PE in 5 consecutive potential-scan cycles. As shown in Fig. 2b, the anodic peak currents decrease with increasing potential scan rates; such results could prove the instability of the modified electrode. Figure 2c shows cyclic voltammograms of AC/THAI-I₂PE in 5 consecutive potential-scan cycles. Figure 2c shows a slight change in the anodic peak potential observed after the first potential scan cycle from 0.50 to 0.52 V; then, the anodic peak potential is constant for 4 potential-scan cycles at about 0.52 V. Also, as shown in Fig. 2c, a slight change in the anodic peak currents was observed; such results could prove the stability of the modified electrode. As shown in Fig. 2c, in a positive scan, an oxidation peak was obtained at about 0.52 V, corresponding to the oxidation of iodide to iodine; at a reversal scan no reduction peak was observed. Based on a Farsang report²⁸ the redox system, I₂/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. Also, when THAI was added, we presumed that both iodide ions (I⁻) and iodine (I₃⁻) may partly from ion-pairs with tetraheptylammonium cations (THA⁺), and are adsorbed on the electrode surface because of the strong affinity of lipophilic carbon paste for THAI. By comparisons of Figs. 2a, 2b and 2c, the affinity of I₃⁻ towards THA⁺ may be much stronger than I⁻ towards it.

The electrochemical behavior of AA (pK_{a1} = 4.17, pK_{a2} = 11.5) is dependent on the pH value of the aqueous solution. Therefore, pH optimization of the solution seems to be necessary

Fig. 2 Cyclic voltammograms of modified paste electrodes. (a) AC/THAIPE. (b) AC/I₂PE in 5 consecutive potential scan cycles. (c) AC/THAI-I₂PE in 5 consecutive potential scan cycles in 0.1 M PBS (pH 2.0) at 100 mV s⁻¹.

in order to obtain the electrocatalytic oxidation of AA. The effect of the pH on the anodic peak potential and the peak current of AA was investigated using cyclic voltammetry. The influence of the solution pH (using PBS buffer) on the peak potential and the current responses of AA at AC/THAI-I₂PE is shown in Fig. 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 are shown in Fig. 3b. The results confirm that the peak currents of AA decreased with increasing buffer solution pH from 2.0 to 7.0, and then increasing with increasing pH up to about 10.0. Also, the anodic peak potentials increased with increasing pH from 2.0 to 10.0. It is well known that AA ($pK_{a1} = 4.17$) exists as a neutral form at pH 2.0. Thus, pH 2.0 was chosen as being optimum.

Figure 4 shows cyclic voltammograms over a potential range from 0.0 to 1.0 V, which is related to different CPE with AC, G,

Fig. 3 (a) Cyclic voltammograms of AC/THAI-I₂PE at various pH values of 2.0 (solid bold line), 4.0 (dashed dot line), 7.0 (dotted line) and 10.0 (dashed line). (b) The effect of pH on the anodic peak current (solid line) and the anodic peak potential (dashed line) of AC/THAI-I₂PE at a scan rate of 100 mV s⁻¹.

G-MWCNT and without carbon. In a positive scan, an oxidation peak was obtained at about 0.48 V for G/THAI-I₂PE, corresponding to the oxidation of iodide to iodine (I⁻/I₃⁻). Also, at a reversal scan, no reduction peak of iodine to iodide (I₃⁻/I⁻) was observed. Under the same condition, an oxidation peak was obtained at about 0.45 V for G-MWCNT/THAI-I₂PE, corresponding to the oxidation of iodide to iodine (I⁻/I₃⁻); also, at a reversal scan, a reduction peak of iodine that formed in the previous scan occurred at nearly 0.26 V. A summary of electrochemical data for the CPEs is given in Table 1. Based on a cyclic voltammogram for G-MWCNT/THAI-I₂PE (Fig. 4, dashed dotted dot line), the potential of the anodic (E_{pa}) and cathodic (E_{pc}) peaks and the half-wave potential ($E_{1/2}$) are 0.451, 0.264 and 0.358 V, respectively. Also, the peak separation potential, ΔE_p ($\Delta E_p = E_{pa} - E_{pc} = 0.187$ V), is greater than the $0.059/n$ V expected for a reversible system; this result suggests that the I⁻/I₃⁻ couple does not act as a reversible system in the G-MWCNT/THAI-I₂PE matrix, and indicates the quasi-reversible monoelectronic charge-transfer process of the I⁻/I₃⁻ couple at paraffin oil-based CPEs. The corresponding reactions of these voltammograms:

Equation (1) includes oxidation of the iodide ion (I⁻) and

Fig. 4 Cyclic voltammograms of ACPE (solid bold line), AC/THAI-I₂PE (dotted line), G/THAI-I₂PE (dashed line) and G-MWCNT/THAI-I₂PE (dashed dotted dot line), in PBS with pH 2.0 at a scan rate of 50 mV s⁻¹ (GCPE and G-MWCNTPE are the same as ACPE, and are not shown in figure).

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

Electrode type	$E_{pa}/$ mV	$E_{pc}/$ mV	$E_{1/2}/$ mV	$\Delta E_p/$ mV	System type
AC/THAI-I ₂ PE	0.525	—	—	—	Irreversible
G/THAI-I ₂ PE	0.480	—	—	—	Irreversible
G-MWCNT/THAI-I ₂ PE	0.451	0.264	0.358	0.187	Quasi-reversible

a. Scan rate, $\nu = 10 \text{ mV s}^{-1}$; pH, 2.0.

reduction of the iodine ion (I₃⁻) with a loss of two electrons in an anodic sweep.

The effect of the scan rate for G-MWCNT/THAI-I₂PE by using cyclic voltammetry is shown in Fig. 5. These cyclic voltammograms were used to examine the variation of the peak current *versus* the sweep rate. Figure 5 shows that the modified electrode had a chemically quasi-reversible redox couple in a PBS (pH 2.0) solution, and that peak currents were increased due to the cyclic voltammetric scan rate. As shown in Fig. 5 (inset), 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, a reversible electron-transfer process at low scan rates.³⁰ It has been suggested that the modified electrode reaction could be a two electron transfer process ($n = 2$). An approximate amount of the electroactive species can be estimated by the method suggested by Sharp *et al.*³¹ for G-MWCNT/THAI-I₂PE. According to this method, the peak current is related to the surface concentration of electroactive species, Γ , following

$$I_p = \frac{n^2 F^2 A \Gamma \nu}{4RT} \quad (2)$$

Hence n represents the number of electrons involved in the reaction, A is the geometric surface area (0.0314 cm²) of the electrode, Γ (mol cm⁻²) is the surface coverage, ν is the scan rate, R (8.314 J mol⁻¹ K⁻¹), F (96485 C mol⁻¹) and T (298 K) denote as usual the gas constant, Faraday constant, and

Fig. 5 Cyclic voltammograms of G-MWCNT/THAI-I₂PE in a 0.1 mol L⁻¹ PBS pH 2.0 at various scan rates: (a) 25, (b) 50, (c) 100, (d) 250, (e) 350, (f) 750 mV s⁻¹. Inset: Plots of the anodic and cathodic peak currents of G-MWCNT/THAI-I₂PE vs. scan rate (ν) from cyclic voltammograms.

temperature, respectively. From the slope (from Fig. 5, inset) of anodic peak currents *versus* scan rate, the surface concentration of CMF was calculated to be $4.27 \times 10^{-8} \text{ mol cm}^{-2}$ for $n = 2$.

Stability and life time of G-MWCNT/THAI-I₂PE

The stability of G-MWCNT/THAI-I₂PE 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-MWCNT/THAI-I₂PE in consecutive 5 potential-scan cycles in PBS at scan rate of 50 mV s⁻¹ (Fig. 6). Only a little change for anodic and cathodic peak currents has been observed and these results could prove the stability of the modified electrode.

Prior to using the G-MWCNT/THAI-I₂PE for the electrocatalytic oxidation of AA, the rate of loss of electrochemical activity for this electrode was investigated. This rate was evaluated by noting the decrease in the anodic charge, q_a , in consecutive potential-scan cycles. The result showed that the anodic and cathodic peak currents of the I/I₃⁻ couple decreased; consequently, the electrochemical activity of G-MWCNT/THAI-I₂PE was reduced during successive scans, without any change in the half-wave potential, $E_{1/2}$. The decrease in the electrochemical

activity may be due to removal of the I^- and I_3^- ions produced at the electrode by dissolution into an aqueous solution. Also, G-MWCNT/THAI- I_2 PE was stable for 2 months. According to

the above results, surface regeneration of the G-MWCNT/THAI- I_2 PE before each experiment is necessary.

Electrocatalytic oxidation of AA at the surface of different PEs

The prime objective of the present work is to determine the concentration of AA using a PE modified electrode. Figure 7 shows CVs obtained for different CPE modified electrodes in 0.1 M PBS pH 2.0 containing 0.5 mM AA. The ACPE, AC/THAI- I_2 PE, G/THAI- I_2 PE and G-MWCNT/THAI- I_2 PE electrodes showed an oxidation wave for 6.9×10^{-4} M AA at 660, 555, 506 and 470 mV (Fig. 7) and a current difference ($\Delta I/\mu A$) for 6.9×10^{-4} M AA 5.5, 3.5, 6.9 and 56.9 μA , respectively. On the other hand, when the G-MWCNT/THAI- I_2 PE electrode was compared with the ACPE, AC/THAI- I_2 PE, G/THAI- I_2 PE electrodes, the oxidation peak potential of AA was shifted to 190, 85 and 36 mV less positive potential. Also, the oxidation current for the G-MWCNT/THAI- I_2 PE electrode was greatly increased in compared with ACPE, AC/THAI- I_2 PE, G/THAI- I_2 PE. The mechanism of this phenomenon can be written as follows:

Fig. 6 Cyclic voltammograms of G-MWCNT/THAI- I_2 PE in 5 consecutive potential-scan cycles in PBS (pH 2.0) at a scan rate of 50 mV s⁻¹.

Fig. 7 Cyclic voltammograms of (a) ACPE, (b) AC/THAI- I_2 PE, (c) G/THAI- I_2 PE and (d) G-MWCNT/THAI- I_2 PE in the absence of AA (solid bold line) in the presence of 6.9×10^{-4} M AA (dashed line) in PBS (pH 2.0) at a scan rate of 50 mV s⁻¹.

These results showed that the electrooxidation of AA to dehydroascorbic acid (DHAA) can be catalyzed by the I^-/I_3^- couple as a mediator at the surface of the modified electrode.

In order to obtain the best composition of the G-MWCNT/THAI- I_2 PE electrode, we used different quantities ratios of G:MWCNT = 1:3, 2:2, 3:1, 3.5:0.5 for the preparation of modified electrodes. For this work, with increasing the MWCNT amount (G:MWCNT = 1:3, 2:2), the anodic peak potential for the G-MWCNT/THAI- I_2 PE electrode was shifted to a positive potential, and with decreasing of the MWCNT amount (G:MWCNT = 3.5:0.5) the anodic peak potential for the G-MWCNT/THAI- I_2 PE electrode was similar to that of the G/THAI- I_2 PE electrode. According to these results, we selected the optimum composition 3:1 (G:MWCNT) in all experimental work.

To understand the fast electron-transfer reaction of AA at the G-MWCNT/THAI- I_2 PE modified electrode quantitatively, we calculated the standard heterogeneous rate constant (k_s) for AA at G-MWCNT/THAI- I_2 PE and bare ACPE electrodes using the Velasco equation, as given below:³²

$$k_s = 1.11 D_o^{1/2} (E_p - E_{p1/2})^{-1/2} \nu^{1/2}, \quad (5)$$

where k_s is the standard heterogeneous rate constant; D_o the apparent diffusion coefficient; E_p the oxidation peak potential; $E_{p1/2}$ the half-wave oxidation peak potential, and ν the scan rate. In order to determine k_s , it is necessary to find the diffusion coefficient for AA. The apparent diffusion coefficient (D_o) value was determined by a single potential chronoamperometry technique based on the Cottrell slope obtained by plotting *versus* $1/\sqrt{\text{time}}$. Chronoamperometry measurements were carried out for AA both at bare ACPE and G-MWCNT/THAI- I_2 PE electrodes. Based on the Cottrell equation, the diffusion coefficient of AA was found to be $5.47 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for the G-MWCNT/THAI- I_2 PE electrode.³³ The estimated standard heterogeneous rate constant (k_s) values for the totally irreversible oxidation of AA both at bare ACPE and G-MWCNT/THAI- I_2 PE electrodes were found to be 1.21×10^{-3} and $9.6 \times 10^{-3} \text{ cm s}^{-1}$, respectively. The obtained higher k_s value for AA at the G-MWCNT/THAI- I_2 PE modified electrode indicated that the oxidation of AA was faster at the G-MWCNT/THAI- I_2 PE electrode than at the ACPE electrode.

Evaluation of the proposed modified electrode

Under the optimum conditions, the determination of AA was carried out at the potential range of 0.1 to 0.9 V using the cyclic voltammetry mode. The AA electro-oxidation peak was observed at potential of about 0.470 V *versus* SCE. The electrocatalytic peak current of AA at the surface of G-MWCNT/THAI- I_2 PE was linearly dependent on the AA concentration. These peak currents were linear up to 0.012 M, described by the equation $\Delta I (\mu\text{A}) = 36436[\text{AA}] + 57.4$, $r = 0.9991$, $n = 12$, where $\Delta I (\mu\text{A})$ is the difference in the oxidation peak currents G-MWCNT/THAI- I_2 PE before and after the addition of AA, $[\text{AA}]$ (M) the AA concentration, r the correlation coefficient and n represents the number of determinations (Fig. 8). The detection limit (3σ) was $3.6 \times 10^{-5} \text{ M}$. The relative standard deviation (RSD %) for 5 determinations of AA with $4.6 \times 10^{-4} \text{ M}$ concentration was 0.6%.

Interference study

For investigating interference, several compounds were selected. If the tolerance limit was taken as the maximum concentration of foreign substances, which caused an

Fig. 8 Cyclic voltammograms of AA at various concentration (from a to m): 0.0, 7.8×10^{-5} , 6.5×10^{-4} , 1.4×10^{-3} , 2.2×10^{-3} , 3.4×10^{-3} , 4.5×10^{-3} , 5.7×10^{-3} , 7.1×10^{-3} , 8.4×10^{-3} , 1.0×10^{-2} and $1.2 \times 10^{-2} \text{ M}$ at surface of the G-MWCNT/THAI- I_2 PE. The solution conditions were pH 2.00 (0.1 M PBS + 0.1 M LiCl). The scan rate was 100 mV s^{-1} .

approximately 5% relative error, for $1.2 \times 10^{-4} \text{ mol L}^{-1}$ AA, no interference was observed for the following compounds: lactose, maleic acid, glycine, maltose, sucrose, fructose, oxalic acid, succinic acid, tartaric acid and glucose. The results are listed in Table 2.

Application in real samples

In order to prove the capability of this modified electrode for the catalytic oxidation of AA in the real samples, we examined this ability in the voltammetric determination of AA in some pharmaceutical preparations and foods. Therefore, pharmaceutical tablet solutions were prepared by accurately weighing and grinding of tablets, and then filtering of any dissolved obtained powder in the working buffer solution. The determination of AA in pharmaceutical preparations was carried by the standard addition method in order to prevent on any matrix effect. The results were compared with those obtained using the official iodometric titration method.³⁴ The paired *t*-test equation, applied in statistics is

$$t = \frac{|\bar{d}\sqrt{n}|}{s_d}, \quad (6)$$

where $\bar{d}$ and s_d are the mean and standard deviation, respectively, of $\bar{d}$ (the difference between paired values). For the pairs of values given in Table 3, the mean difference, $\bar{d}$, 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 the AA concentration.³⁵

Table 2 Effect of diverse substances on the analysis of 1.5×10^{-3} mol L⁻¹ AA

Substance	[Interference substance]/[AA]
Lactose, maleic acid, glycine, maltose	1000
Succharose	500
Fructose	100
Oxalic acid, succinic acid, tartaric acid	50
Glucose	10

Table 3 Determination of AA in real samples with using a G-MW/THAI-I₂PE electrode

Sample	Claimed preparation/ mg	Proposed method ^a / mg (±SD)	Iodine method ^a / mg (±SD)
AA powder	500 per sachet	479.5 (±1.6)	483.2 (±1.2)
AA tablet	250 per tablet	237.8 (±1.8)	242.1 (±1.3)
Egypt's orange (100 ml)	—	87.1 (±1.9)	83.9 (±2.0)
Baluchestan's lemon (100 ml)	—	57.0 (±2.4)	61.3 (±2.0)

a. Results based on five replicate determinations per sample.

Conclusions

The construction of a graphite-multiwall carbon nanotube/tetraheptylammonium iodide-iodine paste electrode and its use for electrocatalytic oxidation and the determination of different concentrations of AA was described. The overpotential was reduced with a value of 190 mV for the oxidation of AA. The experimental conditions, such as pH 2 of the supporting electrolyte, scan rate of 100 mV s⁻¹ and composition of the G-MWCNT/I₂-THAIPE have been used for the determination of AA. To study 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 two methods. A simple fabrication procedure, a wide linear range, high stability and good reproducibility for repeated determinations, suggest this electrode being as a good, cheap and an attractive candidate for practical applications.

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References

1. A. Garrido Frenich, M. E. Hernaa Ndez Torres, A. Belmonte Vega, J. L. Martiane Vidal, and P. Plaza Bolanos, *J. Agric. Food Chem.*, **2005**, 53, 7371.
2. F. E. Harrison and J. M. May, *Free Radical Biol. Med.*, **2009**, 46, 727.
3. M. Khorasani-Motlagh and M. Noroozifar, *Anal. Sci.*, **2003**, 19, 1671.
4. S. Ashok Kumar, P. H. Lo, and S. M. Chen, *Biosens. Bioelectron.*, **2008**, 24, 518.
5. M. Sahin, L. Ozcan, B. Usta, and Y. Sahin, *Biosens. Bioelectron.*, **2009**, 24, 3492.
6. O. Gilbert, B. E. Kumara Swamy, U. Chandra, and B. S. Sherigara, *J. Electroanal. Chem.*, **2009**, 636, 80.
7. M. Noroozifar and M. Khorasani-Motlagh, *Talanta*, **2003**, 61, 173.
8. M. Noroozifar, M. Khorasani-Motlagh, and A. R. Farahmand, *Acta Chim. Slov.*, **2004**, 51, 717.
9. T. Takayanagi, M. Nishiuchi, M. Ousaka, M. Oshima, and S. Motomizu, *Talanta*, **2009**, 79, 1055.
10. M. O. Zyürek, K. Güclü, B. Bektas, and O. Apak, *Anal. Chim. Acta*, **2007**, 588, 88.
11. G. Burini, *J. Chromatogr. A*, **2007**, 1154, 97.
12. L. Wang, L. Zhang, S. She, and F. Gao, *Spectrochim. Acta, Part A*, **2005**, 61, 2737.
13. X. Li and A. A. Franke, *J. Chromatogr. B*, **2009**, 877, 853.
14. A. Sivanesan, P. Kannan, and S. Abraham John, *Electrochim. Acta*, **2007**, 52, 8118.
15. J.-B. Raoof, R. Ojani, R. Hosseinzadeh, and V. Ghasemi, *Anal. Sci.*, **2003**, 19, 1251.
16. R. Takita, K. Yoshida, and J. I. Anzai, *Sens. Actuators, B*, **2007**, 121, 54.
17. T. Rohani and M. A. Taher, *Talanta*, **2009**, 78, 743.
18. A. Merkoci, M. Pumera, X. Llopis, B. Pérez, M. del Valle, and S. Alegret, *Trends Anal. Chem.*, **2005**, 24, 826.
19. M. D. Rubianes and G. A. Rivas, *Electrochem. Commun.*, **2003**, 5, 689.
20. M. Noroozifar and M. Khorasani-Motlagh, *Talanta*, **2003**, 61, 173.
21. A. Kojo and J. Martínez Calatayud, *Anal. Chim. Acta*, **1995**, 308, 334.
22. M. Carlton, M. Hasler, and K. Painter, *Radiochem. Radioanal. Lett.*, **1979**, 39, 19.
23. H. Jansen, R. Jansen, U. A. T. Brinkman, and R. W. Frei, *Chromatographia*, **1987**, 24, 555.
24. J.-B. Raoof, R. Ojani, and S. Rashid-Nadimi, *Electrochim. Acta*, **2004**, 49, 271.
25. R. Akbari, M. Noroozifar, M. Khorasani-Motlagh, and A. Taheri, *Anal. Sci.*, **2010**, 26, 425.
26. B. Nalini and S. S. Narayanan, *Anal. Chim. Acta*, **2000**, 405, 93.
27. Z. Guorong, W. Xiaolei, S. Xingwang, and S. Tianling, *Talanta*, **2000**, 51, 1019.
28. G. Farsang, *Acta Chim. Hung.*, **1965**, 45, 163.
29. I. Svancara and J. Konvalina, *Electroanalysis*, **1998**, 10, 787.
30. L. Fernández and H. Carrero, *Electrochim. Acta*, **2005**, 50, 1233.
31. M. Sharp, M. Petersson, and K. Edstrom, *J. Electroanal. Chem.*, **1979**, 95, 123.
32. J. G. Velasco, *Electroanalysis*, **1997**, 9, 880.
33. A. J. Bard and L. R. Faulkner, *Electrochemical 455 Methods: Fundamentals and Applications*, 2nd ed., **2001**, John Wiley, New York.
34. A. A. Izuagie and F. O. Izuagie, *J. Agric. Biol. Sci.*, **2007**, 3, 367.
35. J. C. Miller and J. N. Miller, *Statistics for Analytical Chemistry*, 2nd ed., **1988**, John Wiley and Sons, New York, 58.