

Electrochemical investigation of *p*-chloranil as an organic mediator in determination of dopamine using of multiwall carbon nanotubes paste electrode

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Abstract: In this work, we study electrochemical behavior of *p*-chloranil as a suitable mediator for voltammetric determination of dopamine (DA) using voltammetric method. Using the modified electrode, the kinetics of DA electrooxidation was considerably enhanced by lowering the anodic over potential through a catalytic fashion. The differential voltammetric peak currents of the electrode increased linearly with the corresponding DA concentration in the range of 0.5-115 $\mu\text{mol L}^{-1}$ with a detection limit of 0.2 $\mu\text{mol L}^{-1}$. The influence of pH and potential interfering substances on the determination of DA were studied. The RSD% for 5 replicates determination of 100 $\mu\text{mol L}^{-1}$ of DA were 1.5%. Finally, the sensor was examined as a selective, simple, and precise new electrochemical sensor for the determination of DA in real samples, such as drug and urine, with satisfactory results.

Keywords: Dopamine; *p*-chloranil; Multi-wall carbon nanotubes paste electrode; Organic mediator; Voltammetry.

Introduction

Dopamine is a catecholamine neurotransmitter that occurs in a wide variety of animals, including both vertebrates and invertebrates. In the brain, this phenethylamine functions as a neurotransmitter, activating the five types of dopamine receptors—D₁, D₂, D₃, D₄, and D₅—and their variants. Dopamine is produced in several areas of the brain, including the substantia nigra and the ventral tegmental area [1]. Dopamine is also a neurohormone released by the hypothalamus. Its main function as a hormone is to inhibit the release of prolactin from the anterior lobe of the pituitary. Dopamine can be supplied as a medication that acts on the sympathetic nervous system, producing effects such as increased heart rate and blood pressure. However, because dopamine cannot cross the blood-brain barrier, dopamine given as a drug does not directly affect the central nervous system.

Therefore, determination of this compound is very important. Consequently, different modified electrodes such as polyvinyl alcohol [2], zirconium phosphated silica gel [3], poly(phenosafranin) [4], cetylpyridinium bromide [5], triazole self-assembled monolayer [6] and cobalt(II) hexacyanoferrate [7], 2,2'-

[3,6-dioxo-1,8-octanediy]bis(nitriloethylidene)]-bis-hydroquinone [8] and single crystal Au(111) [9] have been used for detection of DA alone or in the presence of other species.

Carbon nanotubes (CNT) used building blocks of nanotechnology. With one hundred times the tensile strength of steel, thermal conductivity better than all but the purest diamond, and electrical conductivity similar to copper, but with the ability to carry much higher currents, they seem to be a very interesting material. Since their discovery in 1991 [10], CNTs have generated great interest for future applications based on their field emission and electronic transport properties [11], their high mechanical strength [12] and chemical properties. From it arises an increasing potential for use as field emission devices [13], nanoscale transistors [14], tips for scanning microscopy [15] or components for composite materials [16]. CNT seem to be an interesting material for analysis in general [17] and electroanalysis [18-20] particularly. On other hand, nanosized particles have a chemical behavior similar to small molecules and can be used as specific electrochemical label.

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Nanoparticles may be expected to be superior in several ways. Another hand, Organic compounds with electrochemical activity can be useful as a mediator in determination of biological compounds. Therefore, in this study in continuation of our studies concerning the preparation of chemically modified electrodes [21-24], we described initially the preparation and suitability of a *p*-chloranil modified carbon nanotubes-TiO₂ paste electrode (CAMMWCNTPE) as a new electrocatalyst in the electrocatalysis and determination of DA in an aqueous buffer solution. Finally, in order to demonstrate the catalytic ability of the modified electrode in the determination of DA in real samples, we examined this method for the voltammetric determination of DA in ampoule and urine samples.

Experimental

Apparatus and Reagents

All electrochemical measurements were performed using BHP 2063+ Electrochemical Analysis System, Behpajoo, Iran potentiostat/galvanostat coupled with a Pentium IV personal computer connected with a HP laser jet 6L printer. An Ag / AgCl / KCl 3 M, a platinum wire, and a *p*-chloranil modified multi wall carbon nanotubes and TiO₂ paste electrode (CAMMWCNTPE) were used as reference, auxiliary and working electrodes, respectively. A digital *pH/mV* meter (Metrohm model 710) was applied for pH measurements. Graphite fine powder, paraffin oil, DA and reagents were analytical grade from Merck. Multi-walled carbon nanotubes (purity more than 95%) with o.d. between 10 and 20 nm, *i.d.* between 5 and 10 nm and tube length from 0.5 to 200 nm were prepared from Nanostructured & Amorphous Materials (USA). A 1.0×10^{-3} mol L⁻¹ DA solution was prepared daily by dissolving 0.019 g dopamine hydrochloride in water and the solution was diluted to 100 mL with water in a 100 mL volumetric flask. The solution was kept in a refrigerator at 4 °C and in dark. More dilute solutions were prepared by serial dilution with water.

Phosphate buffer (sodium dihydrogen phosphate and disodium monohydrogen phosphate plus sodium hydroxide, 0.1 mol L⁻¹) solutions (PBS) with different pH values were used.

Preparation of the Electrode

Modified carbon nanotubes paste electrodes were prepared by dissolve 0.01 g of *p*-chloranil in diethyl ether and hand mixing with 84-times its weight of graphite powder, 0.05 g TiO₂ and 10-times its weight of carbon nanotubes with a mortar and pestle. The solvent was evaporated by stirring. A 70:30 (*w/w*)

mixture of *p*-chloranil spiked carbon nanotubes powder and paraffin oil was blended by hand mixing for 20 min until a uniformly-wetted paste was obtained. The paste was then packed into the end of a glass tube. Electrical contact was made by inserting a copper wire into the glass tube at the back of the mixture. When necessary, a new surface was obtained by pushing an excess of paste out of the tube and polishing it on a weighing paper. Unmodified carbon paste, prepared in the same way without adding *p*-chloranil, TiO₂ and carbon nanotubes to the mixture and was used for comparison purposes.

Recommended Procedure

The modified multi-wall carbon nanotubes paste electrode was polished with a white and clean paper. To prepare a blank solution, 10.0 mL of PBD (pH 9.0), was transferred into an electrochemical cell. The initial and final potentials were adjusted to -0.25 and +0.25 V vs. Ag/AgCl respectively. The DPV was recorded to give the blank signal and labeled as I_{pb} . Then different amounts of DA solution were added to the cell, using a micropipette, and the DPV was recorded again to get the analytical signal (I_{ps}). Calibration curves were constructed by plotting the catalytic peak current vs. the DA concentration.

Stability and Reproducibility

The repeatability and stability of the CAMMWCNTPE was investigated by cyclic voltammetry measurements of 100 μmol L⁻¹ DA. The relative standard deviation (*RSD*) for five successive assays is 1.5%. When using four different electrodes, the *RSD* for five measurements is 1.6%. When stored in a laboratory, the modified electrode retains 97% of its initial response after a week and 94% after 45 days. These results indicate that CAMMWCNTPE has good stability and reproducibility, and could be used for DA.

Results and discussion

Electrochemistry of mediator

Ensafi *et al.* have recently constructed CAMMWCNTPE by incorporation of *p*-chloranil into carbon paste matrix and studied its electrochemical properties in buffered aqueous solution by cyclic voltammetry [25]. Its cyclic voltammograms exhibits an anodic ($E_{pa} = 0.08$ V) and corresponding cathodic peaks with $E_{pc} = -0.05$ V vs. Ag|AgCl|KCl_{sat} related to benzoquinone/hydroquinone Q/H₂Q redox couple with quasi-reversible behavior.²⁵ Also, the obtained result

shows that the redox process of Q/H₂Q in *p*-chloranil is dependent on the pH of aqueous solution.

The oxidation behavior of CAMMWCNTPE was studied by cyclic voltammetry using buffer solutions at pH levels ranging from 3.0 to 11.0 at a scan rate of 100 mV s⁻¹. The results showed three linear segments with different slopes in the pH range. At a pH level below 5.5, oxidation of *p*-chloranil occurred with a two

protons transfer and two electrons transfer reaction. For pH values between 5.5 < pH < 8.0, oxidation occurred with a one-proton and a one-electron transfer. Finally, in the pH range of 8.0–11.0, it occurred with a one proton transfer and a four electrons transfer (Figure 1). It was, therefore, concluded that the electrochemical behavior of CAMMWCNTPE was dependent on pH level.

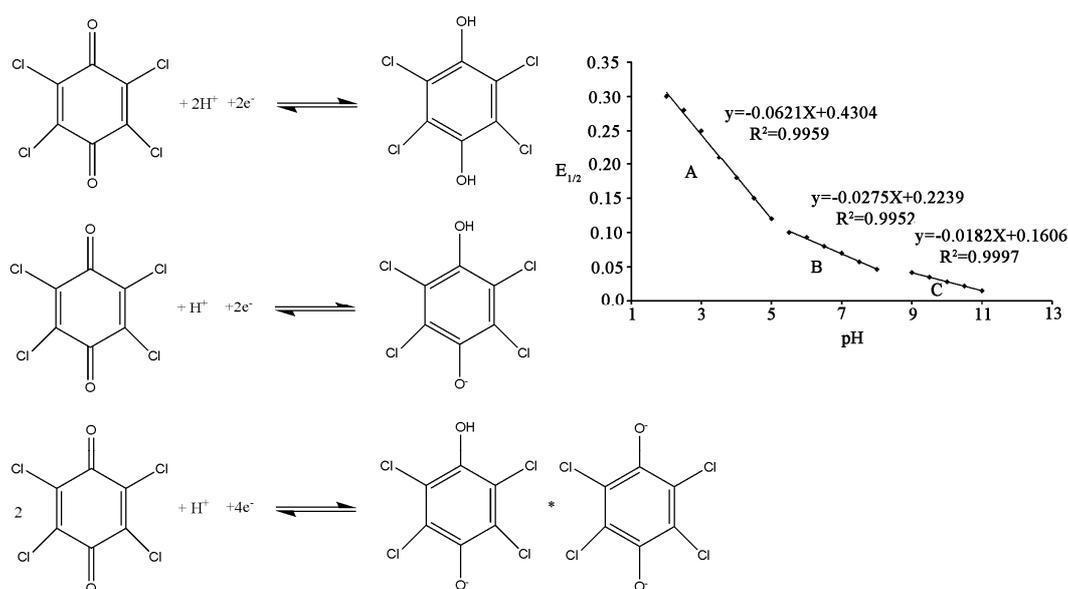


Figure 1. Mechanism of oxidation reduction for *p*-chloranil at different pH values. (Insert): The pH–potential diagram for CAMMWCNTPE.

Consequently, we can assume diffusion controlled behavior for charge transfer at CAMMWCNTPE and use potential-step chronoamperometric experiments to estimate the diffusion coefficient of *p*-chloranil into the paraffin oil used for paste preparation. The slope of the linear region of the $I-t^{-1/2}$ plot in the short time region produces the apparent diffusion coefficient (D_{app}) of the spiked *p*-chloranil into CAMMWCNTPE using Cottrell equation [26]:

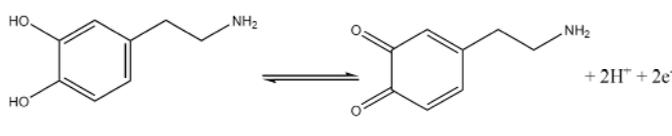
$$I = n F A_g D_{app}^{1/2} C \pi^{-1/2} t^{-1/2} \quad (1)$$

Where C is the known concentration, D_{app} is the apparent diffusion coefficient of spiked *p*-chloranil in paraffin oil and A_g is the geometric area of this electrode (the diameter (d) of the CAMMWCNTPE was measured and then the geometric area of the

CAMMWCNTPE was calculated according to $\pi(d/2)^2$. Therefore, we calculated the apparent diffusion coefficient for *p*-chloranil in carbon paste matrix. It was found that $D = 2.5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$.

pH optimization

It is well known that the electrochemical behavior of DA is dependent on pH value of the aqueous solution, as shown in Scheme 1. On other hand, CA as a mediator for in this work is dependent of pH. Therefore, pH optimization of the solution seems to be necessary in order to obtain the electrocatalytic oxidation of DA. The results showed that the maximum electrocatalytic current was obtained at pH 9.0. Therefore, pH 9.0 was chosen as the optimum pH for the determination of DA at CAMMWCNTPE.



Scheme 1. Oxidation mechanism for dopamine.

Catalytic effect

Cyclic voltammetric responses for the electrochemical oxidation of $300 \mu\text{mol L}^{-1}$ DA at CAMMWCNTPE shows in figure 2 curve d, *p*-chloranil modified carbon paste electrode (CAMCPE) (curve e), carbon nanotubes paste electrode (CNPE) (curve c), and a bare CPE (curve b). As can be seen, the anodic peak potential for the oxidation of DA at CAMMWCNTPE (curve d) and CAMCPE (curve e) is about 100 mV, while it is about 260 mV at the CNPE the bare CPE. From these results, it is concluded that the best electrocatalytic effect for DA oxidation is observed at CAMMWCNTPE. The results show that the peak potential of oxidation at CAMMWCNTPE shifted by about 160 mV toward the negative values compared with those at a CNPE and bare CPE. Similarly, when we compared DA oxidation behaviors at the CAMMWCNTPE and CAMCPE, we found a dramatic enhancement of the anodic peak current at

CAMMWCNTPE relative to the value obtained at the CAMCPE. In other words, the data obtained clearly show that the combination of carbon nanotubes, TiO_2 and the mediator (*p*-chloranil) definitely improve the characteristics of DA oxidation. This behavior is typical of that expected for electrocatalysis at chemically modified electrodes (Scheme 2). Figure 3 shows the relation of anodic peak current (I_{pa}) versus square root of the scan rate ($v^{1/2}$) for $300 \mu\text{mol L}^{-1}$ of DA. The results confirm that anodic peak currents increase linearly with the square root of the scan rate, suggesting that at sufficient over-potential, the reaction is mass transfer controlled. In order to obtain information on the rate-determining step, a Tafel plot was developed for CAMMWCNTPE in presence of DA using the data derived from the raising part of the current-voltage curve. The slope of the Tafel plot is equal to $n(1-\alpha)F/2.3RT$ which comes up to $10.822 \text{ V decade}^{-1}$. Assuming $n = 2$, then $\alpha = 0.68$.

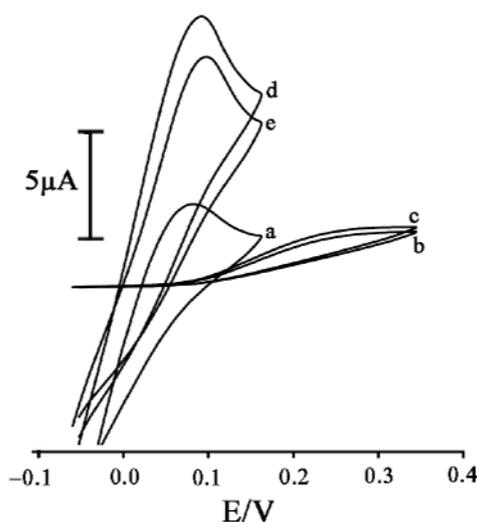
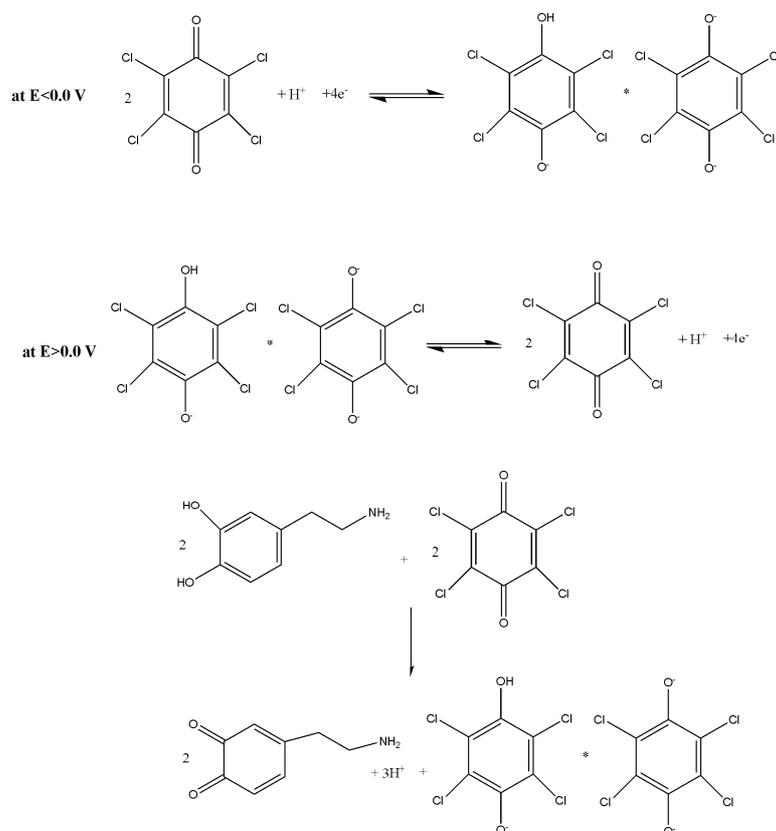


Figure 2. Cyclic voltammograms of 0.1 mol L^{-1} PBS (pH 9.0) with a scan rate of 20 mV s^{-1} for: (a) in the absence and (d): in the presence of $300 \mu\text{mol L}^{-1}$ DA at CAMMWCNTPE. (e) is as (d) at CAMCPE. (c) is as (d) and (b) is as (e) at CNPE and at CPE, respectively.



Scheme 2. Mechanism of the electrocatalytic reaction.

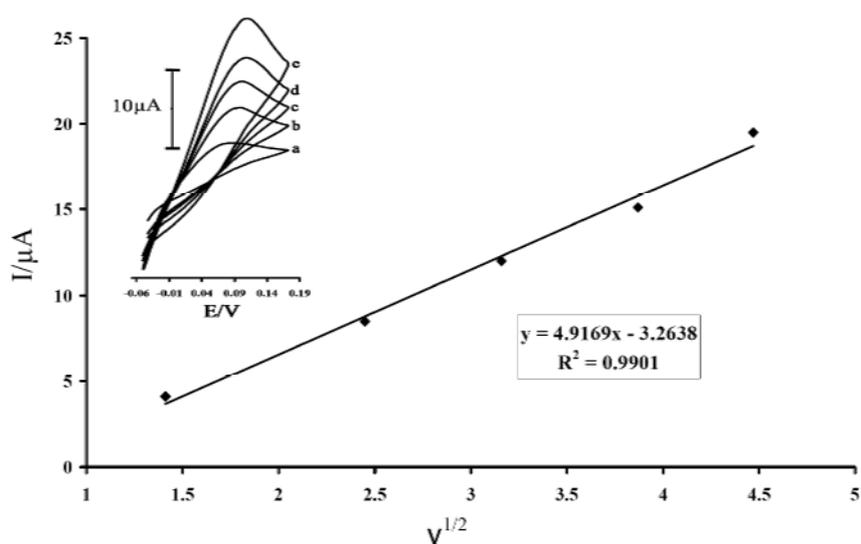


Figure 3. Plot of I_{pa} versus $v^{1/2}$ for the oxidation of DA at CAMMWCNTPE. Insert: Cyclic voltammograms of $300 \mu\text{mol L}^{-1}$ DA at various scan rates: (a) 2; (b) 6; (c) 10; (d) 15 and (e) 20 mV s^{-1} in 0.1 mol L^{-1} PBS (pH 9.0).

In addition, the value of αn_{α} (n_{α} is the number of electrons involved in the rate-determining step) was calculated for the oxidation of DA at pH 9.0 for both CAMMWCNTPE and CNPE using the following equation [27]:

$$\alpha n_{\alpha} = 0.048 / (E_p - E_{p/2})$$

where $E_{p/2}$ is the potential corresponding to $I_{p/2}$. The values for αn_{α} were found to be 0.67 and 0.20 for CAMMWCNTPE and CNPE, respectively. These values show that the over-potential of DA oxidation is reduced at CAMMWCNTPE, and that the rate of electron transfer process is greatly enhanced. This phenomenon is thus, confirmed by the larger I_{pa} values recorded during cyclic voltammetry at CAMMWCNTPE. In addition, with increasing the potential scan rate, the catalytic oxidation peak potential gradually shifts towards more positive potentials, suggesting a kinetic limitation in the reaction between the redox site of the *p*-chloranil and DA.

Chronoamperometric Study

Double step potential chronoamperometry was also employed to the investigation of electrochemical

behavior of aqueous buffered solution (pH 9.00) containing of various concentration of DA at CAMMWCNTPE by setting the working electrode potential at -0.05 V (at the first potential step) and 0.15 V (at the second potential step) vs. Ag|AgCl|KCl_{sat} (Figure 4). As can be seen, there is not any net cathodic current corresponding to the reduction of mediator in the presence of DA, when the potential is stepped from -0.05 V to 0.15 V vs. Ag|AgCl|KCl_{sat}. However, in the presence of DA the charge value associated with forward chronoamperometry is significantly greater than that observed for backward chronoamperometry (Fig. 4. Insert A (b' and c')). The linearity of electrocatalytic current vs. $v^{1/2}$ shows this current is controlled by diffusion of DA from bulk solution toward surface of electrode that caused to near-Cottrellian behavior. Therefore, the slope of linear region of Cottrell's plot can be used to estimate the diffusion coefficient of DA (Fig. 4 insert B). A plot of I versus $t^{1/2}$ for a CAMMWCNTPE in the presence of DA gives a straight line, the slope of such lines can be used to estimate the diffusion coefficient of DA (D) in the ranges of 100-200 $\mu\text{mol L}^{-1}$. The mean value of the D found to be $5.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

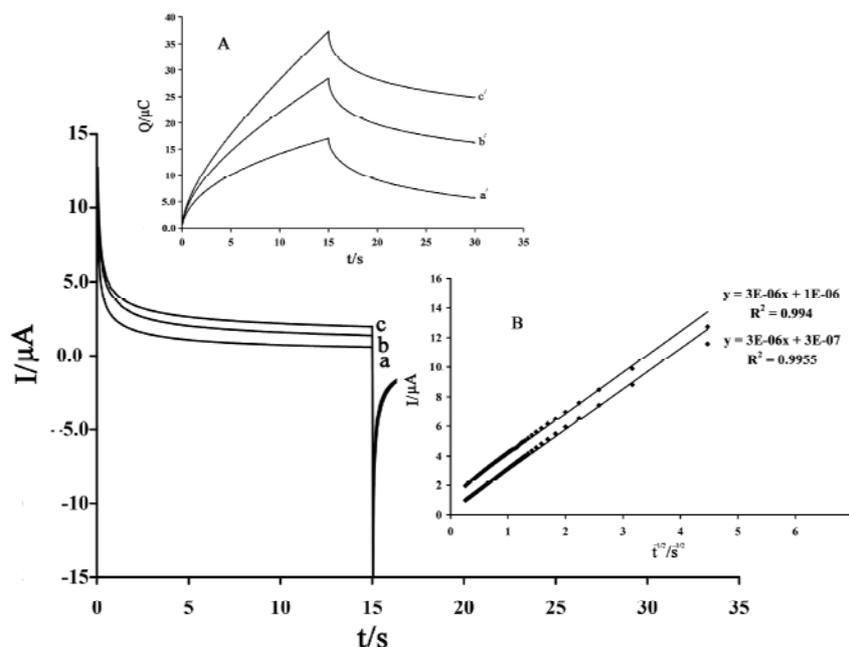


Figure 4. Chronoamperograms obtained at CAMMWCNTPE in the absence a) and in the presence of b) 100 and c) 200 $\mu\text{mol L}^{-1}$ DA at pH 9.0. Insert A) Shows the charge-time curves: (a') for curve (a), (b') for curve (b) and (c') for curve (c). Insert B) Cottrell's plot for the data from the chronoamperograms.

The rate constant for the chemical reaction between DA and redox sites in CAMMWCNTPE, k_h , can be evaluated by chronoamperometry according to the method of Galus [28]:

$$I_C/I_L = \gamma^{1/2} [\pi^{1/2} \operatorname{erf}(\gamma^{1/2}) + \exp(-\gamma)/\gamma^{1/2}] \quad (1)$$

where, I_C is the catalytic current of DA at CAMMWCNTPE, I_L the limited current in the absence of DA, and t is the time elapsed (s). Based on the slope of the I_C / I_L versus $t^{1/2}$ plots, k_h can be obtained for a given DA concentration. Using the values of the slopes, the average value of k_h was found to be $k_h = 2.75 \times 10^2 \text{ mol}^{-1} \text{ L s}^{-1}$. The value of k_h also explains the sharp feature of the catalytic peak observed for the catalytic oxidation of DA at the surface of CAMMWCNTPE.

Dynamic range and detection limit

Since differential pulse voltammetry (DPV) has a much higher current sensitivity and better resolution than cyclic voltammetry, DPV was used for determination of DA (Fig. 5). The results show two linear segments with different slopes for DA concentration; namely, for 0.5 – 14.5 $\mu\text{mol L}^{-1}$ of DA, the regression equation was $I_p(\mu\text{A}) = 0.5025 C_{\text{DA}} + 18.39$ ($r^2 = 0.9927$, $n = 5$), while for 19.5-115 $\mu\text{mol L}^{-1}$ of DA, the regression equation was $I_p(\mu\text{A}) = 0.0999 C_{\text{DA}} + 23.482$ ($r^2 = 0.9946$, $n = 5$), where C_{DA} is $\mu\text{mol L}^{-1}$ concentration of DA. The detection limit was determined at 0.2 $\mu\text{mol L}^{-1}$ DA according to the definition of $Y_{\text{LOD}} = Y_B + 3\sigma$ [29].

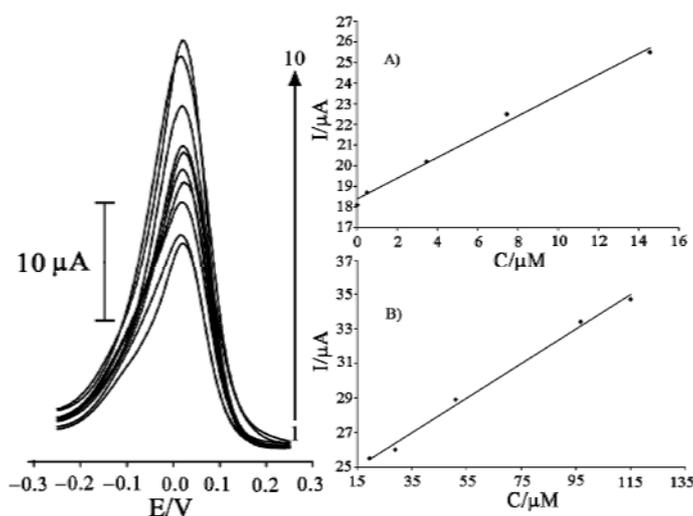


Figure 5. Differential pulse voltammograms at CAMMWCNTPE in (1) absence and presence of (2) 0.5, (3) 3.46, (4) 7.45, (5) 14.5, (6) 19.5, (7) 29, (8) 51, (9) 97, and (10) 115 $\mu\text{mol L}^{-1}$ DA in 0.1 phosphate buffer solution (pH 9.00). Insert A) Plot of electrocatalytic peak current (from DPV) versus DA concentration in range 0.5-14.5 $\mu\text{mol L}^{-1}$ and insert B) as insert A) in range 19.5-115 $\mu\text{mol L}^{-1}$.

Interference Studies

The influence of various substances as compounds potentially interfering with the determination of DA was studied under optimum conditions with 5.0 $\mu\text{mol L}^{-1}$ DA at pH 9.0. The potentially interfering substance was chosen from the group of substances commonly

found with DA in pharmaceuticals and/or in biological fluids. The tolerance limit was defined as the maximum concentration of the interfering substance that caused an error of less than $\pm 5\%$ for the determination of DA. Result shows in Table 1.

Table 1. Interference study for the determination of 5.0 $\mu\text{mol L}^{-1}$ DA under the optimized conditions.

Species	Tolerante limits ($W_{\text{Substance}}/W_{\text{DA}}$)
Urea , Thiourea, SCN^- , CO_3^{2-} , Br^- NH_4^+ ,Glucose , Fructose, Lactose , Sucrose, Ca^{2+} , Mg^{2+} , ClO_4^- , F^- , Cl^-	800
Starch	Saturation
Alanine, Phenylalanine, Methionine, Valine, Tryptophan	200
Ascorbic acid	1

Determination of DA in Real Samples

For determination of DA in dopamine injection we selected 1 mL of the DA injection solution (specified content of DA is 200 mg per 5 mL) was diluted to 50 mL with phosphate buffer, then a 0.8 mL portion of the solution was diluted in a voltammetric cell to 10 mL of 0.1 M phosphate buffer (pH 9.0). The potentials were controlled between -0.25 and 0.25 V. I_{pa} was measured at the oxidation potential of DA by DPV. The average

determination results of DA in the injection were 206 mg/5 mL, which were quite corresponding to the value that was given by injection specification. This experiment was repeated four times and the relative standard deviation obtained was 1.7%. Different standard concentrations of DA were added to the diluted DA injection for testing recovery. The results are shown in Table 2.

Table 2. Determination of DA in ampoule and urine samples.

Sample ^a	Added ($\mu\text{mol L}^{-1}$)	Expected ($\mu\text{mol L}^{-1}$)	Founded ($\mu\text{mol L}^{-1}$) ^a	RSD(%)
1 Ampoule	---	30.0	30.1 ± 0.15	1.72
2	10.0	40.0	40.25 ± 0.21	1.85
3	10.0	50.0	50.53 ± 0.32	1.09
4 Urine	---	---	<detection limit	---
5	20.0	20.0	20.55 ± 0.25	1.90
6	30.0	50.0	50.12 ± 0.32	2.12

^a Average of five replicate measurements.

Conclusion

This work demonstrates the construction of a chemically modified carbon nanotubes and TiO_2 paste electrode by the incorporation of *p*-chloranil as modifying species. This electrode is simple, easy to

prepare and surface renewal is easy. The electrochemical behavior of the *p*-chloranil has been studied by cyclic voltammetry and chronoamperometry in both the absence and presence of DA. The results show that the oxidation of DA is catalyzed at pH 9.0, whereas the peak potential of DA is shifted by 160 mV

to a less positive potential at the surface of the CAMMWCNTPE. Kinetic parameters such as electron transfer coefficient and heterogeneous rate constant for DA was determined using electrochemical approaches. Finally, this modified electrode used for the determination of DA in drug and urine samples.

Acknowledgments

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