Novel poly(3-methylthiophene)/Pd, Pt nanoparticle sensor: Synthesis, characterization and its application to the simultaneous analysis of dopamine and ascorbic acid in biological fluids

Nada F. Atta *, Maher F. El-Kady

Department of Chemistry, Faculty of Science, University of Cairo, 1 Gameaa Al Kahira St., Post Code 12613, Giza, Egypt

ABSTRACT

A promising modified electrode was fabricated by distributing Pt or Pd nanoparticles into conductive polymer matrix of poly(3-methylthiophene) (PMT). Electrochemical investigation of the resulting films was achieved using cyclic voltammetry and differential pulse voltammetry. Several factors affecting the electrocatalytic activity of the hybrid material were studied. Some are related to the polymer such as film thickness, method of its formation and dedoping the polymer film before loading metal particles, other factors are related to the metal particles such as type of metal deposited, method of its deposition, its amount and deposition voltage. EDX analysis was employed to confirm the loading of metal particles to the polymer film. The results suggest that the hybrid film modified electrode combining the advantages of PMT and metal nanoparticles exhibits dramatic electrocatalytic effect on the oxidation of dopamine (DA) and results in a marked enhancement of the current response. The proposed method was applied to the simultaneous determination of ascorbic acid (AA) and dopamine (DA) in physiological pH 7.4 PBS. It was observed that in the presence of AA at millimolar level (0.1 mM), the Pd nanoparticle-modified PMT electrode can sense the increase of DA at micromolar concentration (0.05–1 μM) which is typical of the physiological conditions. The interference study shows that the modified electrode exhibits excellent selectivity in the presence of AA and uric acid (UA) and glucose. It has been shown that this modified electrode can be used as a sensor with high reproducibility, sensitivity, and stability. The method was applied to urine and healthy human blood serum samples and excellent results were obtained.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Conducting polymer incorporated metallic nanoparticles provide an exciting system and hold potential application in electronics, sensors and catalysis [1–5]. It is well known that noble metal-based catalysts are widely used in industry. However, the catalytic activity of these metals is known to depend highly on their dispersion and surface properties. Conducting polymers are often considered to be useful matrices for the immobilization of the dispersed noble metal nanoparticles [6]. The porous structure of conducting polymer allows dispersing the metal particles into the polymer matrix and generates additional electrocatalytic sites [7–9]. Furthermore, the mediation of charge transfer between the substrate and the dispersed metal particles is facile in the matrix of a conducting polymer [1,10–13]. Moreover, the incorporation of metal nanoparticles into conducting polymers provides enhanced performance for both the "host" and the "guest", and this can lead

to different physical properties and important potential applications [14]. Conducting polymer incorporated metallic nanoparticles have synergistic chemical and physical properties based on the constituent polymer and introduced metal [15,16].

Dopamine (DA) is one of the most significant catecholamines and belongs to the family of excitatory chemical neurotransmitters. It plays a very important role in the functioning of the central nervous, cardiovascular, renal and hormonal systems, as well as a key role in drug addiction and Parkinson's disease. Tremendous consideration has been given in biomedically oriented research, to design selective, sensitive and reliable methods for the direct measurement of DA in the presence of interfering molecules [15–20]. Three primary challenges to measure DA under physiological conditions utilizing electrochemical methods still remain: (i) the very low concentration levels of DA (0.01–1 μM) [18], (ii) the intensive interference arising from the electroactive ascorbate (AA) that is present at relatively high concentrations (about 0.1 mM) which results in poor selectivity and sensitivity for DA detection, and (iii) AA is oxidized at almost the same potential as DA [21,22]. As a result, an overlapping voltammetric response for the oxidation of a mixture of DA and AA is obtained.

* Corresponding author. Tel.: +20 0237825266; fax: +20 0235727556.
  E-mail address: Nada_fah1@yahoo.com (N.F. Atta).

On the other hand, ascorbic acid (AA), vitamin C, is known for its reductive properties, being consumed at a wide scale as an antioxidant agent in foods, fruits, vegetables, and soft drinks, besides its importance for therapeutic purposes. As to electrochemical methods, the main problems related to AA determination with bare electrodes lie in the electrode fouling by oxidation products and in the high potential required for AA oxidation [23]. Recent clinical studies have demonstrated that the concentration of ascorbate in biological fluids can be used to assess the amount of oxidative stress in human metabolism [24–26].

Hence there is much interest in the development of reliable methods to quantify AA and DA simultaneously in biological systems. High-performance liquid chromatography (HPLC) with electrochemical detection is often used for the determination of catecholamines and their metabolites [27–30]. The detection of neurotransmitters and their metabolites by electrochemical methods has attracted great interest because of their simplicity, rapidness and high sensitivity, the ability of sensing neurotransmitters in living organisms and in vivo real-time analysis [31]. However, electrochemical analysis on the unmodified electrodes such as glassy carbon (GC), Pt, Au electrodes has limitations because of overlapping voltammetric peaks and high concentrations of ascorbate in typical biological matrices [23]. Recently, attention has been paid to develop a new generation of modified electrodes involving conducting polymers and nanoparticles able to solve efficiently the problems encountered in the conventional unmodified electrodes.

Poly(3-methylthiophene) (PMT) film modified electrodes showed excellent electrocatalytic effect on phenolic compounds [32], catecholamine neurotransmitters [23], amino acids [33], and NADH [34]. Thus, the modification of the PMT films with metal nanoparticles might hopefully promote its electrocatalytic properties resulting in a new sensor with higher sensitivity, reproducibility and lower detection limits. Carbon nanotube modified glassy carbon electrodes was used for the selective determination of dopamine in the presence of ascorbic acid and serotonin by voltammetry [35].

In the current work, a novel modified electrode was fabricated by the electrodeposition of Pt or Pd nanoparticles into PMT film over the surface of Pt electrode. Up to now, there are only relatively limited reports on composites of PMT, such as PMT/γ-cyclodextrin [36] and PMT/ferrocene [37], PMT/carbon nanotubes [38] and PMT/Au nanoparticles [39]. Of recent technological interest, the use of metal particles modified conducting polymers in sensory applications [40–42]. These modified materials allow for better sensitivity and selectivity for the determination of neurotransmitters and proved better than the unmodified conducting polymers [43–45]. For these reasons the properties of conducting polymer–metal nanoparticles are studied here in detail for applications in sensors. Thus, the optimization of the fabrication of the modified electrode has been considered in detail. The new composite electrode combines the properties of PMT to reduce the oxidation potential with the attractive electrocatalytic properties of Pd nanoparticles to promote a fast electron transfer reaction. The application of the proposed sensor for the determination of AA and DA proved excellent. Different parameters relevant to sensors were considered such as the reproducibility, sensitivity, selectivity, stability of the redox signals as well as detection limits. The simultaneous determination of AA and DA in urine and human blood samples is possible without interference.
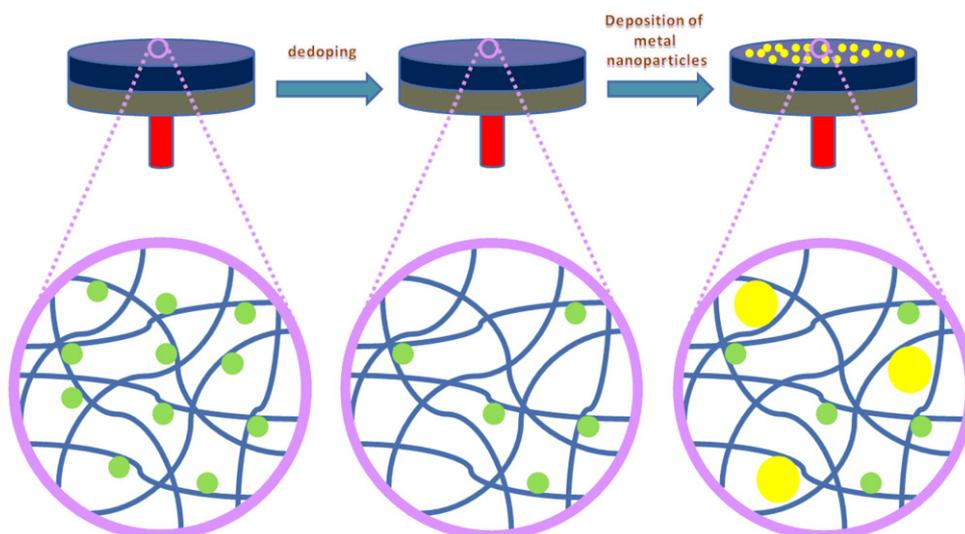
2. Experimental

2.1. Chemicals and reagents

All chemicals were used as received without further purification except 3-methylthiophene which was distilled under rotary evaporator prior to use. 3-Methylthiophene, tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$), acetonitrile (HPLC grade), hydroquinone, dopamine, ascorbic acid, sulfuric acid, and sodium phosphate (mono-, di-, tri-basic salt) were supplied by Aldrich Chem. Co. (Milwaukee, WI, USA). Platinum(II) chloride (Cambridge Chemicals, Oxford, England) and palladium(II) chloride (Scherimg Kaul Paum AG, Berlin, Germany) were also used. Aqueous solutions were prepared using double distilled water.

2.2. Electrochemical cells and equipments

Electrochemical polymerization and characterization were carried out with a three-electrode/one-compartment glass cell. The working electrode was platinum disc (diameter: 1.5 mm). The auxiliary electrode was in the form of 6.0 cm platinum wire. All the potentials in the electrochemical studies were referenced to Ag/AgCl (3.0 M NaCl) electrode. Working electrode was mechanically polished using alumina (2 μm)/water slurry until no visible scratches were observed. Prior to immersion in the cell, the electrode surface was thoroughly rinsed with distilled water and dried.

Scheme 1. Schematic diagram showing the mechanism of undoping and loading of nanoparticles into the polymer matrix.

Highly purified nitrogen was used for oxygen removal by bubbling. All experiments were performed at 25 °C.

The electrosynthesis of the polymers and their electrochemical characterization were performed using a BAS-100B electrochemical analyzer (Bioanalytical Systems, BAS, West Lafayette, USA). JEOL JSM-T330A instrument was used to obtain the scanning electron micrographs of the different films. Philips XL 30 instrument was used to get the EDX results.

2.3. Electrochemical polymerization of PMT films

The electropolymerization of 3-methylthiophene (MT) was achieved in a three-electrode, one-compartment electrochemical cell from a solution containing 0.05 M MT and 0.05 M Bu_4NPF_6 in acetonitrile. The potential applied between the platinum disc working electrode and the reference Ag/AgCl (3.0 M NaCl) is held constant at +1.8 V (Bulk Electrolysis, BE) for different time allowances. The electrode formed in this way is called Pt/PMT(BE). The second alternative is to vary the potential with time, namely 50 mV s^{-1}, between two potential limits, ca. $E_i = -0.1$ V and $E_f = +1.8$ V. The electrode formed in this way is called Pt/PMT(CV). The thickness of the resulting polymer film is therefore controlled by the time elapsed during the electrolysis step or by the number of repeated cycles scanned. Pt/PMT(BE) electrode formed at +1.8 V for 30 s is assumed and Pt/PMT(CV) is formed for 10 cycles in the whole article unless otherwise mentioned.

For all polymer films, the thickness was controlled by the amount of charge consumed during the electropolymerization step. Therefore, assuming 100% current efficiency during the electrochemical conversion, it is possible to use the following empirical equation [46] to roughly estimate the film thickness:

$$L = \frac{m_e j t}{S}$$

where L is the thickness (cm), m_e is the electrochemical equivalent (mg C^{-1}), j is the current density (mA cm^{-2}), t is the time (s), and S is the density (g cm^{-3}). The polymer film was alternatively formed using constant applied potential, $E_{app} = +1.8$ V for 30 and 45 s and the total charge passed was around 1.2×10^4 and 1.8×10^4 μC, respectively. The thickness was calculated to be around 240 and 360 nm for the polymer films formed for 30 and 45 s, respectively. As 100% current efficiency may not be obtained, this represents the maximum film thickness possible and it is constant in all experiments.

2.4. Electrodeposition of Pt or Pd particles

Two trends were followed for electrode modification. In the first one, the polymer film is formed over the Pt substrate and metal nanoparticles were then electrodeposited. In the second trend, metal nanoparticles were electrodeposited directly to the Pt substrate (Scheme 1).

The electrochemical deposition of the metal particles (Pt or Pd) by immersing the electrode in a solution of 2.5 mM PtCl$_2$ or 2.5 mM PdCl$_2$ in 0.1 M HClO$_4$ and a double potential step (BE) or cyclic voltammetric program (CV) is applied to the polymer. In the BE method, a double potential step program was applied to the working electrode according to the following: ($E_i = -0.05$ V, $\Delta t_i = 30$ s, $E_f = +0.01$ V, $\Delta t_f =$ variable). Thus the amount of electrodeposited metal particles was controlled by Δt_f. Unless otherwise mentioned, the time of the second step $\Delta t_f = 300$ s (5 min). The electrode formed in this way is called Pt/PMT/M(BE), M stands for Pt or Pd. The amount of the metal deposited can thus be estimated from the quantity of charge used in the electrodeposition process. The charge passed corresponds to about 5.550×10^{-9} mole/cm^2 (1083 ng/cm^2) of Pt and 6.327×10^{-9} mole/cm^2 (673 ng/cm^2) of Pd deposited.

The cyclic voltammetric (CV) method, on the other hand, involves cycling the potential between −0.25 and +0.65 V at a scan rate of 50 mV s^{-1} and the amount of electrodeposited metal particles was controlled by the number of cycles. Unless otherwise mentioned, 25 cycles were used. The electrode formed in this way is called Pt/PMT/M(CV). The charge passed corresponds to about 5.785×10^{-9} mole/cm^2 (1128 ng/cm^2) of Pt and 6.669×10^{-9} mole/cm^2 (709 ng/cm^2) of Pd deposited.

3. Results and discussion

3.1. Electrocatalytic activity of PMT films

It is common that the properties of polymer-modified electrodes and the catalytic activity of polymers and their composites as modifiers are assessed using the reversible reaction of the hydroquinone/benzoquinone (HQ/BQ) redox couple [6,37]. Fig. 1 shows the cyclic voltammetric (CV) behavior of 5 mM HQ in 0.1 M H$_2$SO$_4$ tested at bare Pt and PMT films formed under different electrochemical conditions, namely, Pt/PMT(BE) and Pt/PMT(CV). It is clear that the oxidation potential shifts to more negative values in the following order Pt, Pt/PMT(CV), Pt/PMT(BE). It is also observed that the oxidation current significantly increases on the polymer-modified electrode. The current increases in the order Pt < Pt/PMT(CV) < Pt/PMT(BE). Moreover, when compared to the response at the bare Pt surface, the oxidation of HQ is more reversible on the polymer-modified surfaces as indicated by the separation between the anodic and the cathodic peak potentials.

However, there are some differences in the electrocatalytic activity between the polymer-modified electrodes which might be explained in terms of the morphological differences between them [1]. SEM micrographs show that Pt/PMT(BE) is compact with low porosity, on the other hand, Pt/PMT(CV) is fluffy with high porosity (as will be discussed later).

3.2. Electrochemical characterization of PMT electrodes modified with Pt or Pd particles

Various papers report the electrochemical properties of nanostructured Pt-modified electrodes in different solutions. This is obviously because most of the electrocatalytic reactions involved in low-temperature fuel cells (i.e., the dioxygen reduction, the dihydrogen oxidation, or the electro-oxidation of small organic molecules, such as methanol and C1 molecules (formaldehyde and formic acid)) occur on Pt and Pt-based catalysts dispersed on a
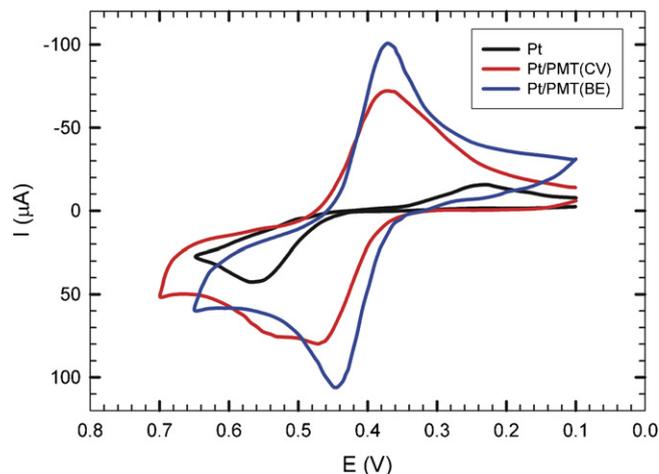

Fig. 1. Cyclic voltammograms obtained at bare Pt, Pt/PMT(BE) and Pt/PMT(CV) electrodes in 5 mM HQ/0.1 M H$_2$SO$_4$. Scan rate = 50 mV s^{-1}.

convenient substrate including conducting polymers [7]. The electrochemical behavior of Pt in sulfuric acid is well known and is described elsewhere [19,47].

On the other hand, the electrochemical properties of Pd nanoparticle-modified conducting polymer electrodes have been considered to a limited extent in literature [43,48]. Pt/Pd and Pt/PMT/Pd electrodes were prepared and tested by cyclic voltammetry in a deaerated solution of 0.1 M H_2SO_4 and the results were compared with bare Pt and Pt/PMT electrodes. The electrodes were cycled in 0.1 M H_2SO_4 solution from 0.1 to 1.0 V (figure not shown here) and broad shoulders (beyond 0.8 V) appear only in Pt/Pd and Pt/PMT/Pd electrodes which can be related to the oxidation of Pd on the surface to palladium oxide (the equilibrium redox potential of Pd/Pd^{2+} is 0.83 V [49]). On the reverse scan (cathodic scan), sharp peaks at about 0.4 V were only observed at Pt/Pd and Pt/PMT/Pd electrodes which can be related to the reduction of Pd previously oxidized in the anodic scan. These results are consistent with recent reports [50,51].

3.3. Optimization of the preparation conditions of PMT film modified with metal particles for sensing applications

3.3.1. The type of electrodeposited metal particles and polymer film thickness

The optimized fabrication of the sensor and the electroactivity of the produced films were studied by using cyclic voltammetry in 5 mM HQ in 0.1 M H_2SO_4. Metal particles (Pd and/or Pt) were electrodeposited on a previously formed PMT polymer film on a Pt electrode. PMT polymer film was prepared using the BE method at +1.8 V for 30 and 45 s in order to vary the polymer film thickness. The metal particles were deposited by double potential step (BE) method. The electrodes formed are thus Pt/PMT(240 nm)/M, Pt/PMT(360 nm)/M; M: Pd and/or Pt. A plot between the percent of Pd in the catalyst feed solution and the corresponding anodic peak current was drawn (Fig. 2A). Several conclusions could be drawn from these results. First of all, the lowest electrochemical activity is for Pt/PMT/Pt and the highest activity is for Pt/PMT/Pd. By changing the composition of the metal loaded, it is observed that as the amount of Pd increases in the feed solution (in comparison to Pt), the current increases reaching its maximum value at 100% Pd. A linear relationship is also observed between the percent of Pd and the anodic peak current for the two polymer films with different thicknesses with a slightly higher slope for the polymer formed for 30 s. The correlation coefficient values are 0.997 and 0.984 for the polymer films formed for 30 and 45 s, respectively. Moreover, it seems that the polymer film thickness has a little effect on the electroactivity of the modified polymer electrodes compared to that of metal particles. This is obvious from the current values and the slopes obtained for the Pt/PMT/M electrode with two different polymer film thicknesses. The current values were similar at constant amount of the metal loaded and the slopes were close to each other in both cases. These results are in agreement with the data obtained in Refs. [52,53]. It is also observed that not only the thicker film has lower slope, but it also has higher capacitive current and less reversibility (for example in Pt/PMT/Pt electrode, it was found that for the thinner film $\Delta E = 75$ mV while it is 89 mV for the thicker film, figure is not shown here). Another important feature is that adding Pd in a small ratio to Pt (e.g. 20% Pd:80% Pt) greatly affects the properties of Pt-modified polymer electrode. It was observed that adding Pd to Pt in Pt/PMT/M film increases the peak current and reduces the potential of oxidation and also improves the reversibility (less peak separation) of the redox reaction. These results are consistent with several previous studies in the literature [54]. It can also be concluded that Pd-modified polymer electrodes have the highest current and therefore the highest catalytic activity for the electro-oxidation of HQ.
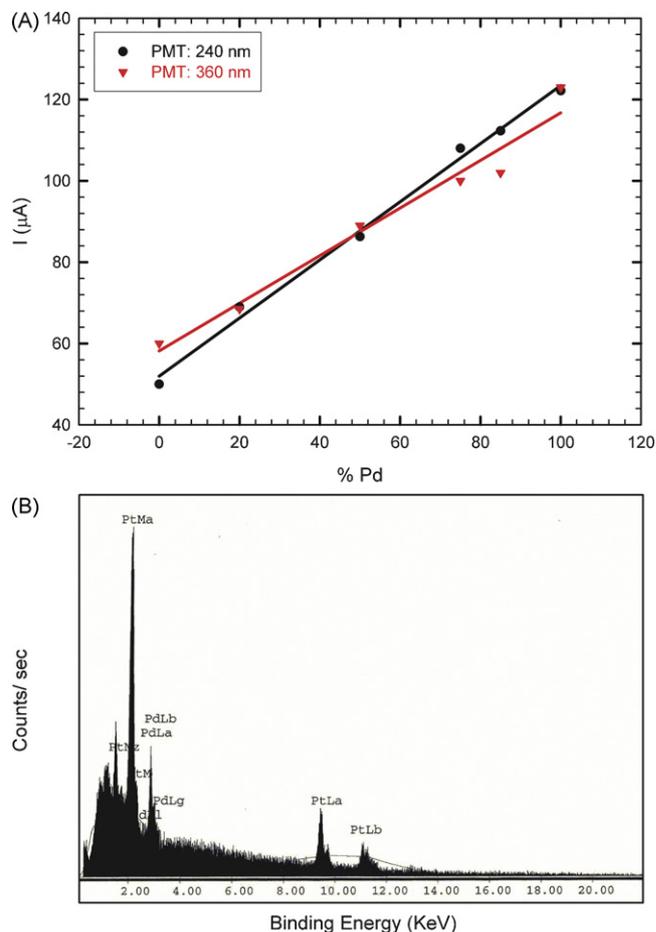

Fig. 2. Effect of the polymer film thickness and ratio of Pd in the (Pt + Pd) loaded particles on the electroactivity of the resulting films: (A) the relationship between the percent of Pd in the feed solution and the anodic peak currents for both polymer films with different thicknesses, Pt/PMT(240 nm)/M, Pt/PMT(360 nm)/M and (B) energy dispersive analysis by X-ray, EDAX, for Pt/PMT/(Pd + Pt) electrode. Pd and Pt were deposited by the double potential step method from a solution of 2.5 mM $PdCl_2$ + 2.5 mM $PtCl_2$/0.1 M $HClO_4$.

In order to check that the ratio of Pd/Pt loaded to the polymer film corresponds to its value in the feed solution, an energy dispersive X-ray analysis (EDX) was performed. Metals were loaded to Pt/PMT electrode from a solution that contained equimolar amounts of $PdCl_2$ and $PtCl_2$ in the feed solution. EDX analysis (Fig. 2B) gave the atomic percents 47.22, 52.78 for Pd and Pt, respectively which is in close agreement with their ratio in the feed solution.

3.3.2. Amount of electrodeposited metal particles

Two methods were used for the electrodeposition of Pd particles: double potential step and cyclic voltammetric methods described in Section 2. In the BE method, Fig. 3A shows the plot of the anodic peak currents of 5 mM HQ against the time of the second step ($\Delta t_f = 1$–12 min) of continuous electrodeposition of Pd particles on Pt/PMT(BE) and bare Pt electrodes (Pt/PMT(BE)/Pd(BE) and Pt/Pd(BE) electrodes are formed) and the results were compared. The results indicate an increase in current with increasing amounts of Pd reaching the maximum at 5 min. Increasing the time of deposition further leads to a decrease in the peak current associated with an increase in the capacitive current and in the peak separation (i.e., lower reversibility). Thus, the optimum deposition time for Pd is 5 min. It can also be noticed that Pt/PMT(BE)/Pd(BE) shows higher catalytic oxidation of DA when compared to Pt/Pd(BE) electrode. In addition, these results can be explained in terms of the
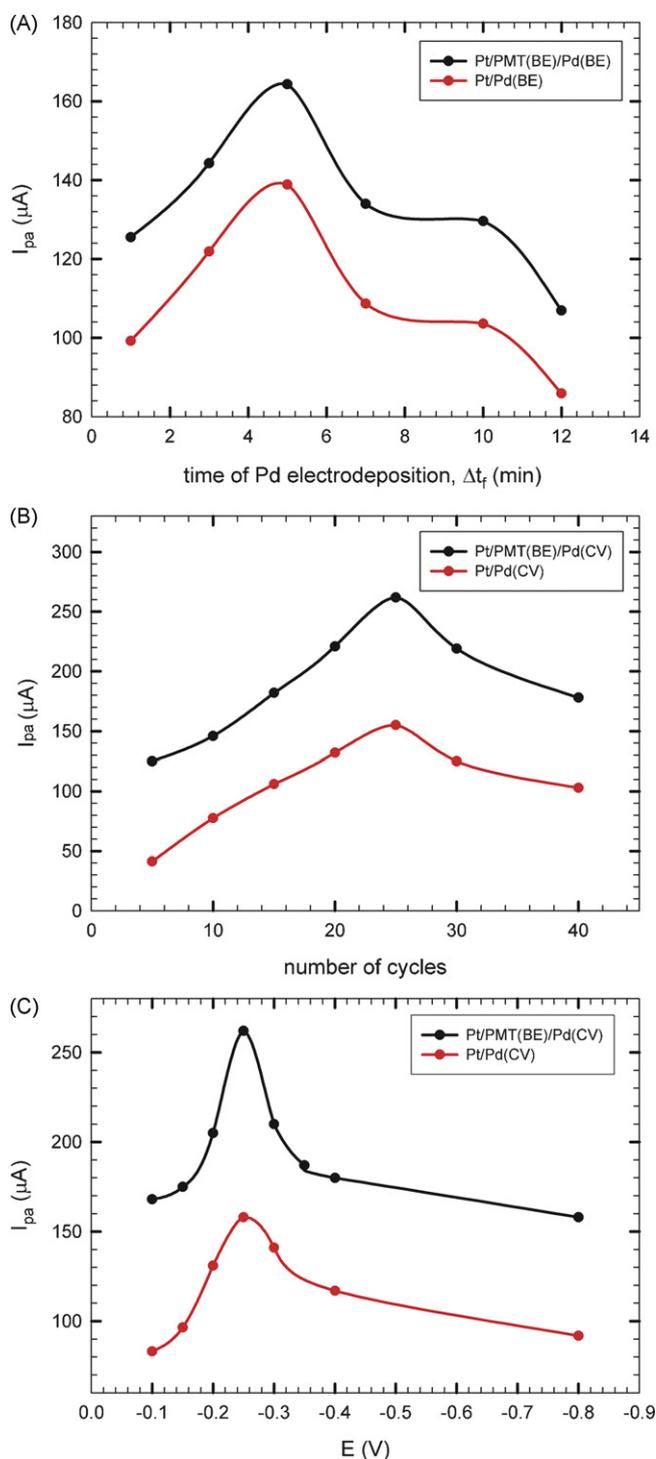
Fig. 3. Different parameters affecting the amount and properties of loaded metal particles: the electrode is formed with the indicated method and tested by CV in 5 mM HQ/0.1 M H$_2$SO$_4$. CV conditions: E_i = +0.1 V, E_f = +0.65 V and scan rate = 50 mV s^{-1}. (A) Effect of the time of deposition of metal particles (ΔE_f) in the double potential step (BE) method, (B) effect of the number of cycles of metal particles deposition in the cyclic voltammetric program (CV) method, and (C) effect of the potential of deposition used in the CV method.

increase in the surface area of the catalyst. The morphology and size of the catalyst should also affect the electrocatalytic efficiency that will be indicated later in the surface morphology studies.

In the CV method, Fig. 3B shows the anodic peak currents of 5 mM HQ against the number of cycles of continuous electrodeposition of Pd particles on Pt/PMT(BE) and bare Pt electrodes (Pt/PMT(BE)/Pd(CV) and Pt/Pd(CV) electrodes are formed) and the

results were compared. From the results, the optimum number of cycles for the electrodeposition of Pd particles was estimated as 25 cycles. Similar results were obtained for Pt electrodeposition [19]. It can also be noticed that Pt/PMT(BE)/Pd(CV) shows higher electrocatalytic activity towards the oxidation of HQ compared to Pt/Pd(CV). Moreover, a comparison of the results of Fig. 3A and B indicates that the electrodeposition of Pd particles with the CV method gives higher electrocatalytic activity with respect to the BE method.

3.3.3. The deposition potential of metal particles

The deposition potential affects not only the amount of catalyst deposited but also its morphology which is an inherent characteristic of the electroactive surfaces [55]. Fig. 3C shows the effect of changing the potential of Pd deposition on the electroactivity of the resulting films. Pd was electrodeposited by the CV method and the deposition potential was controlled by changing the negative limit of the applied potential window so that the potential is cycled between +0.65 V and the other limit is changed between −0.1 and −0.8 V. Results show that the current of electro-oxidation of HQ increases from −0.1 V reaching its maximum value at −0.25 V and then decreases again to −0.8 V. Furthermore, changing the negative limit of the potential window to more negative values (moving from −0.1 to −0.8 V) leads to an increase in the capacitive current, and to an increase in the peak separation and shifts the potential of oxidation of hydroquinone to more positive values. Moreover, almost the same trend was observed when electrodepositing Pd directly over Pt electrode.

3.3.4. The method of electropolymerization of PMT

Fig. 4A shows how changing the method of polymer film formation could affect the electroactivity of Pt/PMT/Pd electrodes. The results indicate that Pt/PMT(BE)/Pd(CV) electrode shows lower oxidation potential, higher oxidation current and lower peak separation and thus is more electroactive in this sense when compared to Pt/PMT(CV)/Pd(CV) electrode. Hence, the method of formation of the polymer film greatly affects the synergistic electrocatalytic effect of the Pt/PMT/Pd composites.

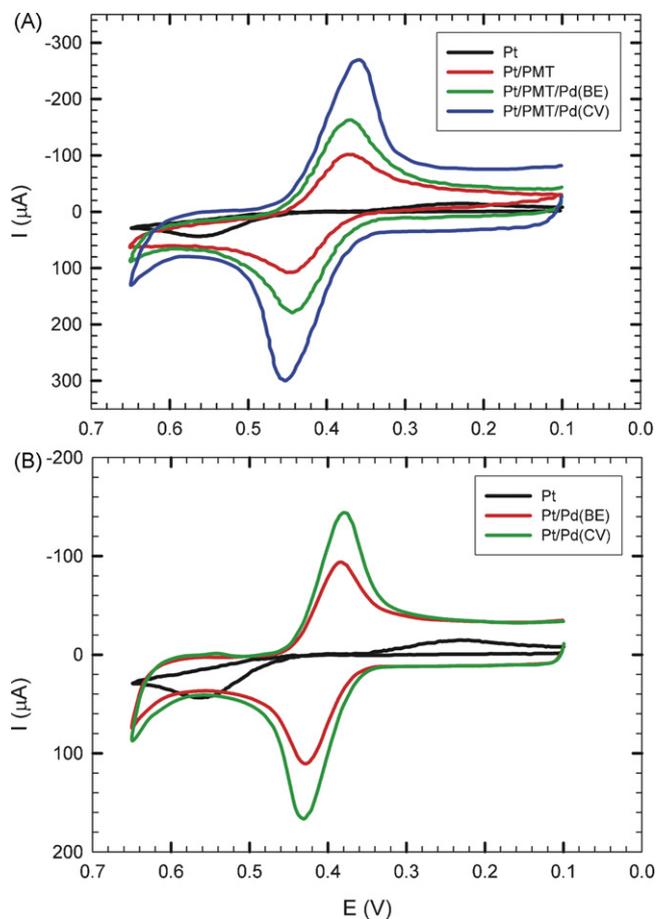### 3.3.5. Doped versus dedoped PMT polymer films

In spite of the importance of the doping level on the conductivity of conducting polymers [41], quite a few articles were published on the effect of the doping level on the electrocatalytic activity of conducting polymer/metal nanoparticle composite electrodes. The PMT film was synthesized using the BE method and washed with acetonitrile. The polymer film was then dedoped in monomer free solution (0.05 M Bu$_4$NPF$_6$/CH$_3$CN) at −0.2 mV for 1 min. Pd particles were then loaded by the CV method (see Scheme 1). The resulting Pd-modified PMT electrode was tested using cyclic voltammetry in 5 mM HQ and the results were compared with the corresponding cases in which the polymer film is doped in Fig. 4B. Dedoping the polymer film before loading Pd particles has the effects of decreasing the current response and increasing the peak separation as well as broad oxidation peaks. Since reorganization of polymer chains should accompany the inclusion (doping) and expulsion (dedoping) of the given anion, the relatively broad oxidation peaks observed at the dedoped films are attributed to the effect caused by the structural differences. Furthermore, the more complicated process during the dedoping process was also observed for poly(pyrrole) [56]. This was attributed to further conformational changes taking place in the polymer. Thus, the doping level has a great effect on the electroactivity of the Pt/PMT, Pt/PMT/Pd electrodes towards the electro-oxidation of HQ.

Fig. 5A shows the cyclic voltammograms of the bare Pt, Pt/PMT, Pt/PMT/Pd(BE), and Pt/PMT/Pd(CV) electrodes tested in 5 mM HQ. A shift of around 119 and 107 mV to more negative potentials was
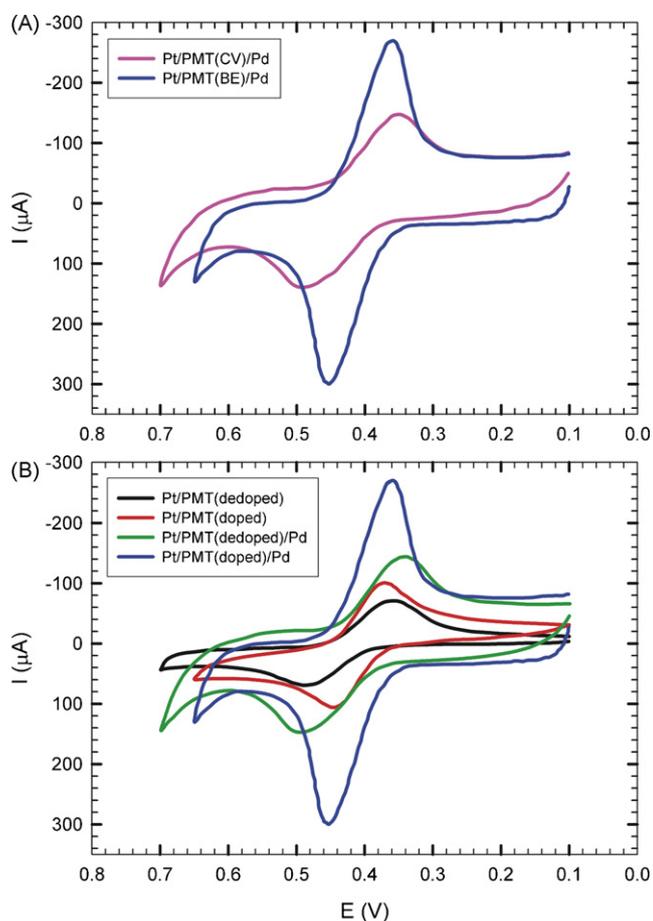
Fig. 4. Effect of the method of PMT formation (A) and doping level of PMT films (B) on the electroactivity of the produced PMT–Pd hybrid. The electrodes are tested in 5 mM HQ/0.1 M H_2SO_4 at a scan rate of 50 mV s^{-1}.

Fig. 5. Comparison between the different electrodes formed by the electrodeposition of Pd on PMT films (A) and directly to Pt (B). Cyclic voltammograms obtained by testing the electrodes in 5 mM HQ/0.1 M H_2SO_4 solution at a scan rate of 50 mV s^{-1}.

observed for Pt/PMT(BE)/Pd(BE), Pt/PMT(BE)/Pd(CV) electrodes, respectively, when compared to bare Pt electrode. 3.88-fold and 6.18-fold enhancements of peak currents were also observed at the same electrodes, respectively. The decrease in the over-potential and enhancement of peak current indicate that the Pt/PMT/Pd electrode can efficiently catalyze the electro-oxidation of HQ. Furthermore, the same trend was also observed when the Pd particles deposited on the bare Pt electrode (Pt/Pd(BE) and Pt/Pd(CV) electrodes) (Fig. 5B). A remarkable enhancement in the current response followed by a drop in peak potential provides a clear evidence of the catalytic effect of Pd particles which act as a promoter to enhance the electrochemical reaction, considerably accelerating the rate of electron transfer. The difference in the electrocatalytic behavior between Pt/PMT(BE)/Pd(BE) and Pt/PMT(BE)/Pd(CV) could be accounted for from the analysis of their morphologies (Fig. 6C–E). SEM micrographs show that the

Pd particles are smaller and homogenously distributed at the latter electrode, while larger Pd particles with dendrite shapes are observed at the previous electrode. This confirms that the size and homogeneity of the deposited particles affect the electroactivity of these modified electrodes [57,58].

3.4. Comparison between Pd and Pt nanoparticle-modified electrodes

Table 1 shows a comparison between Pt- and Pd-modified electrodes towards the electro-oxidation of HQ and the results are compared to bare (bulk) Pt. The electrocatalytic efficiency (measured by the anodic peak current) of the modified electrodes was estimated and compared to bulk Pt electrode. In all cases the Pt- and Pd-modified electrodes show lower oxidation potential and higher oxidation currents compared to bulk Pt electrode. A shift of

Table 1
Comparison between the electroactivity of Pt- and Pd-modified electrodes towards the electro-oxidation of 5 mM HQ/0.1 M H_2SO_4. PMT film was formed by the BE method at +1.8 V for 30 s. Data are taken from CVs.

Electrode type	M = Pd				M = Pt			
	E_{pa} (mV)	ΔE (mV)	I_{pa} (μA cm^{-2})	Current increase[a]	E_{pa} (mV)	ΔE (mV)	I_{pa} (μA cm^{-2})	Current increase[a]
Pt	562	335	42.4	1.00	562	335	42.5	1.00
Pt/M(BE)	429	45	99.5	2.35	438	53	62.8	1.48
Pt/M(CV)	431	51	155.0	3.67	438	60	87.9	2.07
Pt/PMT/M(BE)	443	72	164.0	3.88	448	75	75.4	1.78
Pt/PMT/M(CV)	455	95	262.0	6.18	446	73	142.0	3.34

[a] Normalized to the current obtained at bare Pt.
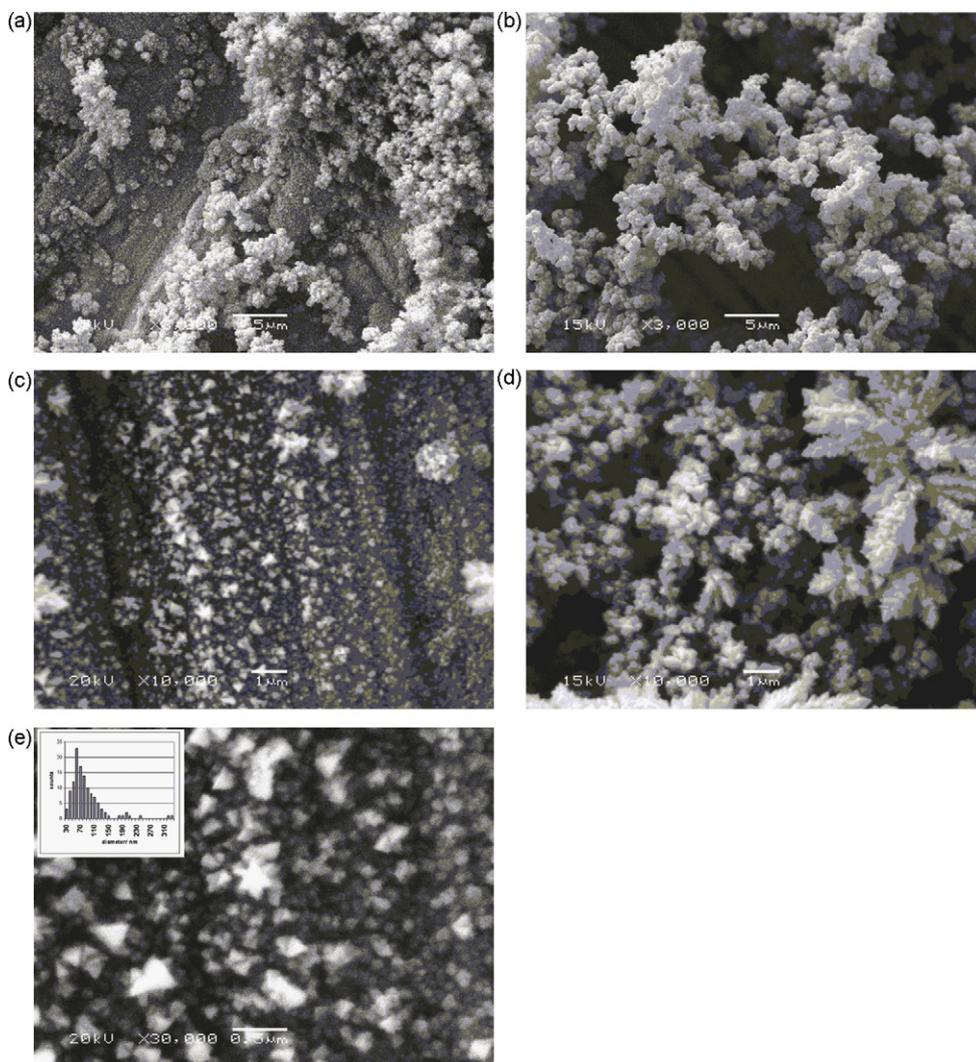
Fig. 6. Scanning electron micrographs for (A) Pt/PMT(BE), (B) Pt/PMT(CV), (C) Pt/PMT(BE)/Pd(BE), and (D) and (E) Pt/PMT(BE)/Pd(CV). Inset: histogram showing the Pd particle size distribution, average size is around 60 nm.

around 124 mV to more negative potentials was observed at Pt/Pt electrodes when compared to bare (bulk) Pt electrode. The current magnitude observed for mM HQ at bulk Pt is smaller when compared to Pt/Pt or Pt/PMT/Pt electrodes. From these observations it is evident that the electrocatalytic responses of the Pt/Pt, Pt/PMT/Pt and bulk Pt electrodes are completely different which indicates that Pt nanoparticles promote the electron transfer between HQ and electrode.

It is also observed that Pd-modified electrodes show lower oxidation potentials and higher peak currents compared to Pt modified and bulk Pt electrodes. This indicates that the redox reaction of the HQ/BQ couple is thermodynamically and kinetically more favorable at the Pd-modified electrodes compared to all other electrodes. Again, a remarkable enhancement in the current response followed by a drop in the peak potential provides a clear evidence of the catalytic effect of Pd particles which act as a promoter to enhance the electrochemical reaction, considerably accelerating the rate of electron transfer.

3.5. Effect of pH on the electrochemistry of DA at Pd-modified electrode

The redox system should be affected by changes in pH because of the involvement of protons in the overall electrode reaction.

The effect of changing the pH of the medium on the response of electrodes was examined in phosphate buffers. Fig. 7 shows the cyclic voltammograms of 5 mM dopamine (DA) in 0.1 M phosphate buffer of varying the pH at Pt/PMT(BE)/Pd(CV) electrode. As illus-
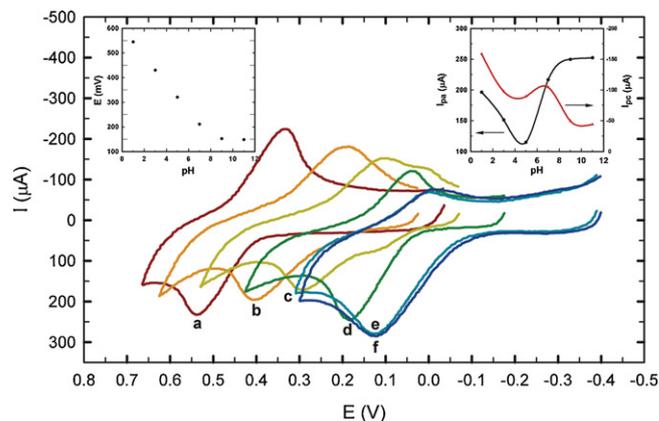
Fig. 7. Effect of solution pH on the electrochemical behavior of Pt/PMT(BE)/Pd(CV) electrode: the electrode is tested in 5 mM DA/0.1 M phosphate buffer solution of different pH values and CVs are shown. Inset (A), dependence of the anodic peak potential of DA oxidation on the solution pH. Inset (B), dependence of the anodic and cathodic peak currents of DA oxidation on solution pH.
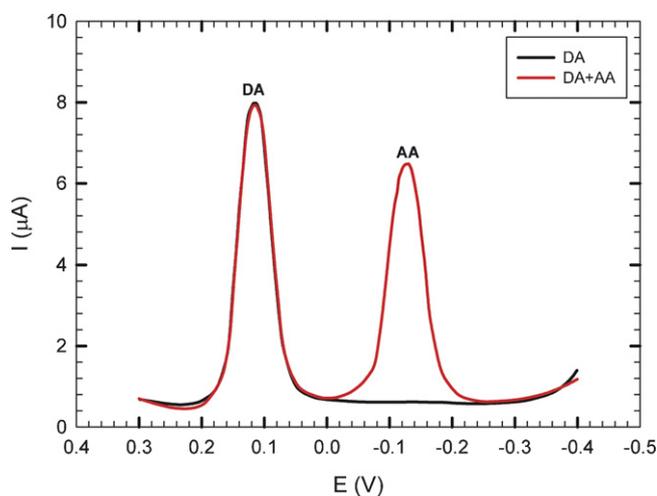
Fig. 8. DPVs for 1 μM DA and 100 μM AA + 1 μM DA at Pt/PMT(BE)/Pd(CV) electrode in 0.1 M pH 7.4 PBS. DPV conditions: pulse amplitude = 50 mV, scan rate = 20 mV s^{-1}, sample width = 17 ms, and pulse width = 50 ms.

trated in Fig. 7 (inset A) the anodic peak potential shifts linearly to more negative values as pH increases over a range from 1 to 7. The slope is −55.6 mV/pH unit. The nearly Nernstian slope obtained here suggests two-proton, two-electron process for dopamine oxidation [59–61]. According to the Nernst equation, the slope of −55.6 mV/pH reveals that the proportion of the electron and proton involved in the reactions is 1:1. As the dopamine oxidation is a two-electron process, the number of protons involved is also predicted to be two. In the solution, the pK_a values of dopamine are 8.9 (pK_{a1}) and 10.6 (pK_{a2}) [62], respectively. A linear behavior for pH values in the range from 1 to 7 and a little deviation at pH 9 were observed. This indicates the deprotonation of DA at pH 9 so that it is no longer a two-proton, two-electron process and at this point other equilibria should be taken into account. At pH 11 the redox reaction of DA is no longer pH dependent as DA is completely deprotonated at this pH. Fig. 7 (inset B) shows that from pH 1 to 5 the anodic peak current decreases with increasing solution pH value 5. DA exists in the protonated form at low pH values. The current of oxidation increases abruptly as the pH increases from 5 to 7. Further, beyond pH 7 the current increases with pH but at a lower rate.

3.6. Differential pulse voltammetry of a mixture of AA and DA

It is well known that ascorbic acid (AA) coexists with dopamine (DA) in the extracellular fluid of the central nervous system and its concentration is much higher than that of DA, so AA is the major interference for DA detection. The ability to selectively determine these species has been a major goal of electroanalysis research. Fig. 8 shows the differential pulse voltammograms (DPVs) of 1.0 μM DA in the absence and presence of 100.0 μM AA at Pt/PMT(BE)/Pd(CV) in phosphate buffer solution (PBS) with the physiological pH of 7.4. Broad overlapped oxidation peak (not shown here) was obtained at bare Pt electrode, but, at Pt/PMT(BE)/Pd(CV) electrode, two well-defined oxidation peaks were obtained at −125 and +115 mV for AA and DA, respectively. It was cited that for a given concentration of DA, a comparatively large oxidation current was noticed in the presence of AA at conventional electrodes [63]. This is due to the fact that oxidation product of DA, dopamine-o-quinone, catalytically reacts with AA and reduces the dopamine-o-quinone back to DA [63]. Therefore, the concentration of DA could not be determined accurately in the presence of AA. However, in the present investigation, the oxida-
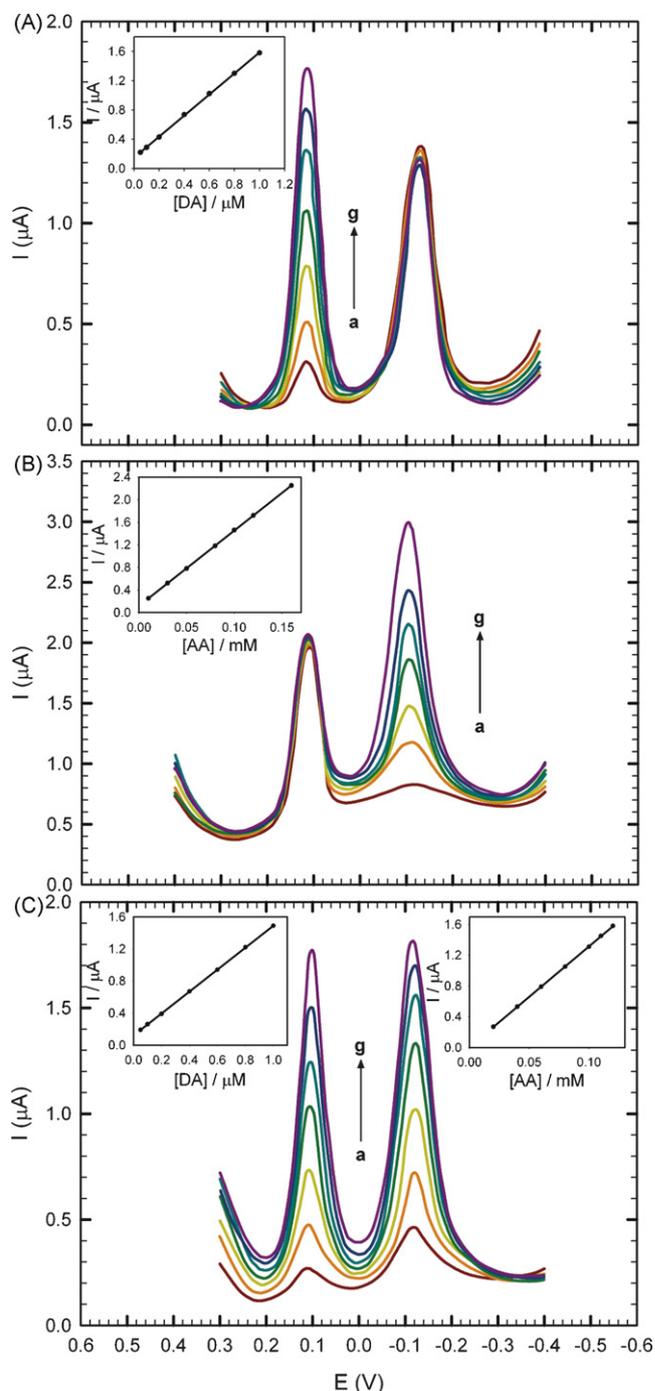
Fig. 9. (A) DPVs of DA at Pt/PMT(BE)/Pd(CV) in the presence of 0.1 mM AA in PBS, pH 7.4. DA concentrations (from a to g): 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 μM. (B) DPVs of AA at Pt/PMT(BE)/Pd(CV) in the presence of 1.0 μM DA in PBS, pH 7.4. AA concentrations (from a to g): 0.01, 0.03, 0.05, 0.08, 0.1, 0.12, and 0.16 mM. (C) DPVs obtained during the simultaneous change of AA and DA at Pt/PMT(BE)/Pd(CV) in PBS, pH 7.4. DA contents (from a to g): 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 μM. AA contents (from a to g): 0.02, 0.04, 0.06, 0.08, 0.1, 0.11, and 0.12 mM. DPV conditions: pulse amplitude = 50 mV, scan rate = 20 mV s^{-1}, sample width = 17 ms, and pulse width = 50 ms.

tion potential and peak currents for DA are almost the same in the presence or absence of AA. What's more, Pt/PMT(BE)/Pd(CV) exhibited the bigger response for the oxidation of DA compared to AA, the oxidation of AA was effectively suppressed so that even 100 times AA had nearly no interference for the determination of DA.

3.6.1. Selective determination of DA in the presence of a fixed large concentration of AA

One of the main objectives of the present investigations is to determine DA in the presence of high concentrations of AA by using Pt/PMT(BE)/Pd(CV) electrode. Fig. 9A exhibits the DPVs that were obtained for the micromolar concentrations (0.05–1 μM) of DA in the presence of 0.1 mM AA at Pt/PMT(BE)/Pd(CV) electrode. The voltammetric peak corresponding to the oxidation of DA was found to be increasing linearly in consonance with the increase of the bulk concentration of DA whereas the peak current for oxidation of AA remained almost constant. Obviously, the responses of AA are unaltered with the increasing DA contents. Thus, the homogeneous catalytic oxidation of AA by the oxidized product of DA can be eliminated at Pt/PMT(BE)/Pd(CV) electrode. It is to be noted that in the presence of AA at millimolar level (0.1 mM), the Pt/PMT(BE)/Pd(CV) can sense the increase of DA at micromolar concentration (0.05–1 μM) which is close to the physiological condition. The calibration plot (Fig. 9A, inset) was linear with a correlation (r^2) of 0.9993 and a sensitivity of 1.44 μA/μM. The detection limit of DA (S/N = 3) is 8 nM.

3.6.2. Selective determination of AA in the presence of DA

On the other hand, to verify the facility of the Pt/PMT(BE)/Pd(CV) electrode for the selective determination of AA in the presence of DA, DPVs were recorded for varying concentrations of AA at a fixed concentration of DA (Fig. 9B). The catalytic peak current of AA changes linearly with its concentration over the range 0.01–0.16 mM with a correlation (r^2) of 0.9991 and a sensitivity of 0.0133 μA/μM (Fig. 9B, inset). The detection limit of AA (S/N = 3) is 7 μM.

3.6.3. Simultaneous determination of AA and DA

Fig. 9C shows DPVs that were obtained at the Pt/PMT(BE)/Pd(CV) electrode during the simultaneous change of the concentrations of AA and DA. They demonstrated that the calibration curves for AA and DA were linear for a wide range of concentrations from 0.02 to 0.12 mM for AA and from 0.05 to 1 μM for DA. This corresponds to the typical concentration ranges of AA and DA in real samples [18]. The calibration plots (Fig. 9C, insets) had the slopes (sensitivities) of 0.0131 and 1.37 μA/μM and correlations (r^2) of 0.9988 and 0.9991, for AA and DA, respectively. The detection limits (S/N = 3) were 6 μM for AA and 9 nM for DA. Interestingly the peak current for DA increased linearly with the increase of DA concentration, while for AA, the peak current too increased linearly but at a slower rate. This phenomenon could have occurred due to the reason that the diffusion of DA through the polymer film was faster compared to that of AA [45]. It is very interesting to note that the detection limits of DA in the absence and presence of AA are virtually the same, which indicates that the oxidation processes of DA and AA at Pt/PMT(BE)/Pd(CV) electrode are independent and that the simultaneous or independent measurements of AA and DA are possible without interference.
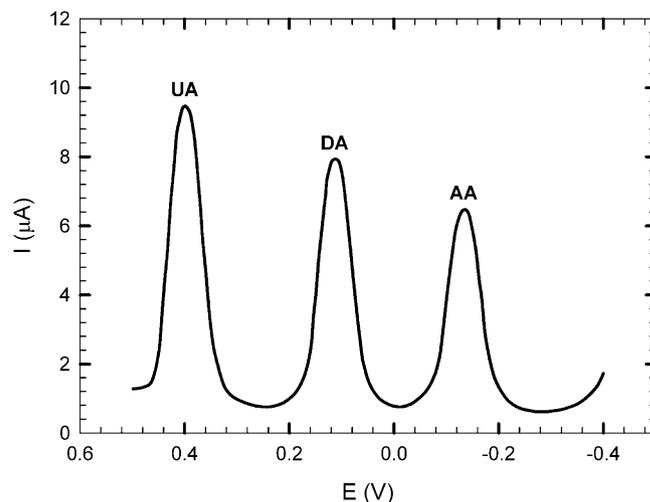

Fig. 10. DPVs for 100 μM AA + 1 μM DA + 1 μM UA at Pt/PMT(BE)/Pd(CV) electrode in 0.1 M pH 7.4 PBS. DPV conditions: pulse amplitude = 50 mV, scan rate = 20 mV s^{-1}, sample width = 17 ms, and pulse width = 50 ms.

3.7. Interference study

Influence of uric acid (UA) on the voltammetric determination of AA and DA is well known as they are oxidized at the same potential [21,22]. Hence, this investigation further extended, on the verification of UA effect on the AA and DA oxidation at Pt/PMT(BE)/Pd(CV) electrode (Fig. 10). It can be seen that the modified electrode resolved the merged voltammetric peak into three well-defined peaks at potentials around −128 mV, +113 mV and +400 mV for AA, DA and UA, respectively. This separation is large enough to allow the simultaneous determination of these three compounds in a homogenous solution. The other main interferences were examined and it was found that 1.0 mM glucose acid did not interfere with 1 μM oxidation.

3.8. Reproducibility and stability of the Pt/PMT(BE)/Pd(CV) electrode

For a novel method, reproducibility of the results is very important. In order to examine the reproducibility of the modified electrode, repeated cyclic voltammetric experiment was run in 10 μM DA in 0.1 M pH 7.4 PBS. The relative standard deviation (R.S.D.) was about 3% after 50 successive CVs indicating that the designed sensor had an excellent reproducibility. After measurement, the modified electrode was cleaned with voltammetric cycles in pH 10.0 PBS to eliminate the adsorption and stored in air. The modified electrode retained 95% of its initial response up to 1 week.

3.9. Real sample analysis

The proposed method was applied to the simultaneous determination of AA and DA in urine and healthy human blood serum

Table 2
Recovery results obtained for AA and DA in urine and healthy human serum samples at the Pt/PMT(BE)/Pd(CV) electrode.

Sample type	Sample no.	Spike		Found		Recoveries (%)	
		AA (mM)	DA (μM)	AA (mM)	DA (μM)	AA	DA
Urine	1	0.05	0.05	0.049	0.048	98	96
	2	0.1	0.1	0.103	0.099	103	99
	3	0.2	1.0	0.208	1.03	104	103
Serum	1	0.05	0.05	0.0488	0.0482	97.6	96.4
	2	0.1	0.1	0.1	0.98	100	98
	3	0.2	1.0	0.203	1.02	101.5	102

Table 3
Analytical parameters for simultaneous detection of AA and DA at several modified electrodes.

Electrode	pH	Studied interferences	Dynamic range (μM)	Limit of detection (nM)	Sensitivity (μA μM^{-1})	Determination in real samples	Reference
GC/Nf/Pt$_{nano}$	7.4	AA, UA, 5-HT	3–60	10	–	DHI, blood plasma	[19]
GC/poly(4-aminothiophenol)/Au$_{nano}$	7.0	AA, UA	0.01–1	–	0.22	DHI, blood serum	[17]
GC/PEDOT/Au$_{nano}$	7.4	AA, UA	0.002–0.02	2	200	–	[16]
GC/PEDOT/Au$_{nano}$	7.4	AA	0.002–0.022	2	6.5–8.5	–	[15]
GC/overoxidized polypyrrole/Au nanoclusters	7.0	AA, 5-HT	0.075–20	15	5.92	Blood serum	[18]
CPE/carbon nanofibers/Pd$_{nano}$	4.5	AA, UA	0.5–160	200	–	DHI	[20]
GC/PAN/PDDMAC/Au$_{nano}$	7.4	–	50–1000	50,000	0.00062	–	[68]
GC/PAN/AgCl core–shell nanocomposites	7.0	AA	0.6–3.6	–	0.49	–	[69]
Pt/polyfuran/Pd$_{nano}$	1.2	AA, UA, ACOP	0.5–100	48	0.4784	–	[44]
GC/Pd$_{nano}$	7.0	AA	8–88	–	0.3147	DHI	[51]
GC/PtAu$_{nano}$	4.0	AA, UA	24–384	24,000	0.05	DHI	[70]
GC/Au$_{nano}$	7.0	AA	15–135	9200	0.0407	DHI	[71]
CPE/CNT/Ag$_{nano}$	2.0	AA	0.8–64	300	–	Human serum	[72]
Pt/PMT/Pd$_{nano}$	7.4	AA, UA	0.05–1	9	1.37	Urine, blood serum	This work

DHI: dopamine hydrochloride injection, GC: glassy carbon electrode, CPE: carbon paste electrode, CNT: carbon nanotube, ACOP: acetaminophen, 5-HT: serotonin, Nf: nafion, PDDMAC: poly(diallyldimethylammoniumchloride), PAN: polyaniline, and PEDOT: poly(3,4-ethylenedioxythiophene).

using the standard addition method. The urine and serum samples were diluted 50 and 100 times, respectively, with 0.1 M pH 7.4 PBS before measurements to prevent the matrix effect of real samples, respectively. Then appropriate amounts of these diluted samples were transferred to the electrochemical cell for the determination of each species using DPV. The results obtained are listed in Table 2. In urine samples, the AA and DA concentrations were found to be 0.13 mM and 1.42 μM, respectively. This is close to those values reported elsewhere [64,65]. On the other hand, the AA concentration in the serum sample was found to be 0.114 mM which is close to the value reported by Yang et al. [66] and Goyal et al. [67]. In our test, no DA was detected in healthy blood serum, when the DA standard solution was spiked; the presence of AA, UC and some interference, such as albumin and glucose did not interfere with the determination of DA. The recoveries indicate that the accuracy and repeatability of the proposed voltammetric method are very good.

Finally, Table 3 shows the comparison chart for the selective determination of dopamine at palladium nanoparticle-modified PMT electrode with various metal nanoparticles based literature reports.

4. Conclusions

The electrochemical synthesis and characterization of Pd-modified Pt and PMT electrodes have been achieved. The method of polymer film formation, doping level of the polymer film, the amount of deposited metal, method of its deposition and deposition potential were found to have a great impact on the electroactivity of the polymer/metal hybrid electrodes. Moreover, Pd-modified electrodes showed excellent electrocatalytic activity compared to Pt-modified electrodes. The proposed method was applied to the simultaneous determination of AA and DA in physiological pH 7.4 PBS. It is very interesting to note that the detection limits of DA in the absence and presence of AA are virtually the same, which indicates that the oxidation processes of DA and AA at Pt/PMT(BE)/Pd(CV) electrode are independent and that the simultaneous or independent measurements of AA and DA are possible without interference. It has been shown that this modified electrode can be used as a sensor with high reproducibility, sen-sitivity, selectivity, and stability. The proposed method could be applied to the determination of AA and DA in real samples without interference.

References

[1] A. Kitani, T. Akashi, K. Sugimoto, S. Ito, Electrocatalytic oxidation of methanol on platinum modified polyaniline electrodes, Synth. Met. 121 (2001) 1301–1302.
[2] A. Drelinkiewicz, M. Hasik, M. Kloc, Pd/polyaniline as the catalysts for 2-ethylanthraquinone hydrogenation. The effect of palladium dispersion, Catal. Lett. 64 (2000) 41–47.
[3] N.F. Heinig, N. Kharbanda, M.R. Pynenburg, X.J. Zhou, G.A. Schultz, K.T. Leung, The growth of nickel nanoparticles on conductive polymer composite electrodes, Mater. Lett. 62 (2008) 2285–2288.
[4] K.R. Reddy, K.-P. Lee, Y. Lee, A.I. Gopalan, Facile synthesis of conducting polymer–metal hybrid nanocomposite by in situ chemical oxidative polymerization with negatively charged metal nanoparticles, Mater. Lett. 62 (2008) 1815–1818.
[5] A.Z. Ernst, S. Zoladek, K. Wiaderek, J.A. Cox, A. Kolary-Zurowska, K. Miecznikowski, P.J. Kulesza, Network films of conducting polymer-linked polyoxometalate-modified gold nanoparticles: preparation and electrochemical characterization, Electrochim. Acta 53 (2008) 3924–3931.
[6] A. Malinauskas, Electrocatalysis at conducting polymers, Synth. Met. 107 (1999) 75–83.
[7] A. Wieckowski, E.R. Savionova, C.G. Vayenas (Eds.), Catalysis and Electrocatalysis at Nanoparticle Surfaces, Marcel Dekker, 2003 (Chapter 25).
[8] L. Zhang, M. Wan, Polyaniline/TiO$_2$ composite nanotubes, J. Phys. Chem. B 107 (2003) 6748–6753.
[9] P. Santhosh, A. Gopalan, K.P. Lee, Gold nanoparticles dispersed polyaniline grafted multiwall carbon nanotubes as newer electrocatalysts: preparation and performances for methanol oxidation, J. Catal. 238 (2006) 177–185.
[10] L. Niu, Q.H. Li, F.H. Wei, X. Chen, H. Wang, Formation optimization of platinum-modified polyaniline films for the electrocatalytic oxidation of methanol, Synth. Met. 139 (2003) 271–276.
[11] A. Frydrychewicz, S.Y. Vassiliev, G.A. Tsirlina, K. Jackowska, Reticulated vitreous carbon–polyaniline–palladium composite electrodes, Electrochim. Acta 50 (2005) 1885–1893.
[12] Z.A. Hu, X.L. Shang, Y.Y. Yang, C. Kong, H.Y. Wu, The electrochemical synthesis of polyaniline/polysulfone composite films and electrocatalytic activity for ascorbic acid oxidation, Electrochim. Acta 51 (2006) 3351–3355.
[13] J.M. Kinyanjui, N.R. Wijeratne, J. Hanks, D.W. Hatchett, Chemical and electrochemical synthesis of polyaniline/platinum composites, Electrochim. Acta 51 (2006) 2825–2835.

[14] R. Gangopadhyay, A. De, Conducting polymer nanocomposites: a brief overview, Chem. Mater. 12 (2000) 608–622.
[15] S.S. Kumar, J. Mathiyarasu, K.L. Phani, Exploration of synergism between a polymer matrix and gold nanoparticles for selective determination of dopamine, J. Electroanal. Chem. 578 (2005) 95–103.
[16] J. Mathiyarasu, S. Senthilkumar, K.L.N. Phani, V. Yegnaraman, PEDOT–Au nanocomposite film for electrochemical sensing, Mater. Lett. 62 (2008) 571–573.
[17] A.I. Gopalan, K.-P. Lee, K.M. Manesh, P. Santhosh, J.H. Kim, J.S. Kang, Electrochemical determination of dopamine and ascorbic acid at a novel gold nanoparticles distributed poly(4-aminothiophenol) modified electrode, Talanta 71 (2007) 1774–1784.
[18] J. Li, X. Lin, Simultaneous determination of dopamine and serotonin on gold nanocluster/overoxidized-polypyrrole composite modified glassy carbon electrode, Sens. Actuators B: Chem. 124 (2007) 486–493.
[19] T. Selvaraju, R. Ramaraj, Electrochemically deposited nanostructured platinum on nafion coated electrode for sensor applications, J. Electroanal. Chem. 585 (2005) 290–300.
[20] J. Huang, Y. Liu, H. Hou, T. You, Simultaneous electrochemical determination of dopamine, uric acid and ascorbic acid using palladium nanoparticle-loaded carbon nanofibers modified electrode, Biosens. Bioelectron. 24 (2008) 632–637.
[21] S.B. Khoo, F. Chen, Studies of sol–gel ceramic film incorporating methylene blue on glassy carbon: an electrocatalytic system for the simultaneous determination of ascorbic and uric acids, Anal. Chem. 74 (2002) 5734–5741.
[22] P. Shakkthivel, S.-M. Chen, Simultaneous determination of ascorbic acid and dopamine in the presence of uric acid on ruthenium oxide modified electrode, Biosens. Bioelectron. 22 (2007) 1680–1687.
[23] H.B. Mark, N. Atta, Y.L. Ma, K.L. Petticrew, H. Zimmer, Y. Shi, S.K. Lunsford, J.F. Rubinson, A. Galal, The electrochemistry of neurotransmitters at conducting organic polymer electrodes: electrocatalysis and analytical applications, Bioelectrochemistry 38 (1995) 229–245.
[24] G.N. Bijur, M.E. Ariza, C.L. Hitchcock, M.V. Williams, Antimutagenic and promutagenic activity of ascorbic acid during oxidative stress, Environ. Mol. Mutagen. 30 (1997) 339–345.
[25] E. Shohami, E. BeitYannai, M. Horowitz, R. Kohen, Oxidative stress in closed-head injury: brain antioxidant capacity as an indicator of functional outcome, J. Cereb. Blood Flow Metab. 17 (1997) 1007–1019.
[26] I. Koshiishi, T. Imanari, Measurement of ascorbate and dehydroascorbate contents in biological fluids, Anal. Chem. 69 (1997) 216–220.
[27] M. Tsunoda, Recent advances in methods for the analysis of catecholamines and their metabolites, Anal. Bioanal. Chem. 386 (2006) 506–514.
[28] E. Sastre, A. Nicolay, B. Bruguerolle, H. Portugal, Method for simultaneous measurement of norepinephrine, 3-methoxy-4-hydroxyphenylglycol and 3,4-dihydroxyphenylglycol by liquid chromatography with electrochemical detection: application in rat cerebral cortex and plasma after lithium chloride treatment, J. Chromatogr. B 801 (2004) 205–211.
[29] W. Zhang, F. Wan, J. Gu, S. Ai, J. Ye, K. Yamamoto, L. Jin, In vivo determination of tetrahydrobiopterin and monoamine neurotransmitters in rat brain by liquid chromatography with a nano crystalline Mn-doped lead dioxide film modified electrode, Chromatographia 59 (2004) 677–682.
[30] B.A. Durgbanshi, S.C. Broch, M.G. Agustí, M. Peiró, J. Romero, Direct injection analysis of epinephrine, norepinephrine, and their naturally occurring derivatives in serum by micellar liquid chromatography with electrochemical detection, J. Liq. Chromatogr. Relat. Technol. 28 (2005) 3265–3281.
[31] B.J. Venton, R.M. Wightman, Psychoanalytical electrochemistry: dopamine and behavior correlating neurochemical changes in the brain with behavior marks the beginning of an exciting new interdisciplinary field, psychoanalytical chemistry, Anal. Chem. 75 (2003) 414A–421A.
[32] A.J. Downard, A.D. Roddick, A.M. Bond, Covalent modification of carbon electrodes for voltammetric differentiation of dopamine and ascorbic acid, Anal. Chim. Acta 317 (1995) 303–310.
[33] L. Agui, A. Gonzalez-Cortes, P. Yanez-Sedeno, J.M. Pingarron, Continuous monitoring of amino acids and related compounds with poly(3-methylthiophene)-coated cylindrical carbon fiber microelectrodes, Anal. Chim. Acta 401 (1999) 145–154.
[34] N.F. Atta, A. Galal, A.E. Karagozler, J.F. Rubinson, H. Zimmer, H.B. Mark Jr., Voltammetric studies of the oxidation of reduced nicotinamide adenine dinucleotide at a conducting polymer electrode, J. Chem. Soc. Chem. Commun. 19 (1991) 1347–1349.
[35] M.C. Rodriguez, M.D. Rubianes, G.A. Rivas, Highly selective determination of dopamine in the presence of ascorbic acid and serotonin at glassy carbon electrodes modified with carbon nanotubes dispersed in polyethylenimine, J. Nanosci. Nanotechnol. 11 (2008) 6003–6009.
[36] D. Bouchta, N. Izaoumen, H. Zejli, M. Kaoutit, K.R. Temsamani, A novel electrochemical synthesis of poly-3-methylthiophene-γ-cyclodextrin film: application for the analysis of chlorpromazine and some neurotransmitters, Biosens. Bioelectron. 20 (2005) 2228–2235.
[37] A. Galal, Electrocatalytic oxidation of some biologically important compounds at conducting polymer electrodes modified by metal complexes, J. Solid State Electrochem. 2 (1998) 7–15.
[38] H.-S. Wang, T.-H. Li, W.-L. Jia, H.-Y. Xu, Highly selective and sensitive determination of dopamine using a nafion/carbon nanotubes coated poly(3-methylthiophene) modified electrode, Biosens. Bioelectron. 22 (2006) 664–669.

[39] X. Huang, Y. Li, Y. Chen, L. Wang, Electrochemical determination of nitrite and iodate by use of gold nanoparticles/poly(3-methylthiophene) composites coated glassy carbon electrode, Sens. Actuators B: Chem. 134 (2008) 780–786.
[40] R.T. Ahuja, D. Kumar, Recent progress in the development of nano-structured conducting polymers/nanocomposites for sensor applications, Sens. Actuators B: Chem. 136 (2009) 275–286.
[41] N.K. Guimard, N. Gomez, C.E. Schmidt, Conducting polymers in biomedical engineering, Prog. Polym. Sci. 32 (2007) 876–921.
[42] B.A. Rozenberg, R. Tenne, Polymer-assisted fabrication of nanoparticles and nanocomposites, Prog. Polym. Sci. 33 (2008) 40–112.
[43] P. Santhosh, K.M. Manesh, S. Uthayakumar, S. Komathi, A.I. Gopalan, K.-P. Lee, Fabrication of enzymatic glucose biosensor based on palladium nanoparticles dispersed onto poly(3,4-ethylenedioxythiophene) nanofibers, Bioelectrochemistry 75 (2009) 61–66.
[44] N.F. Atta, M.F. El-Kady, A. Galal, Palladium nanoclusters-coated polyfuran as a novel sensor for catecholamine neurotransmitters and paracetamol, Sens. Actuators B: Chem. 141 (2009) 566–574.
[45] N.F. Atta, M.F. El-Kady, Poly(3-methylthiophene)/palladium sub-micro-modified sensor electrode. Part II. Voltammetric and EIS studies, and analysis of catecholamine neurotransmitters, ascorbic acid and acetaminophen, Talanta 79 (2009) 639–647.
[46] N.F. Atta, I. Marawi, K.L. Petticrew, H. Zimmer, H.B. Mark, A. Galal, Electrochemistry and detection of some organic and biological molecules at conducting polymer electrodes. Part 3. Evidence of the electrocatalytic effect of the heteroatom of the poly(heteroarylene) at the electrode/electrolyte interface, J. Electroanal. Chem. 408 (1996) 47–52.
[47] W.S. Li, L.P. Tian, Q.M. Huang, H. Li, H.Y. Chen, X.P. Lian, Catalytic oxidation of methanol on molybdate-modified platinum electrode in sulfuric acid solution, J. Power Sources 104 (2002) 281–288.
[48] A.A. Athawale, S.V. Bhagwat, P.P. Katre, Nanocomposite of Pd–polyaniline as a selective methanol sensor, Sens. Actuators B: Chem. 114 (2006) 263–267.
[49] A.J. Bard, L.R. Faulkner, Electrochemical Methods, Fundamentals and Applications, John Wiley & Sons, Inc., 1980.
[50] V.C. Diculescu, A.M.C. Paquim, O. Corduneanu, A.M.O. Brett, Palladium nanoparticles and nanowires deposited electrochemically: AFM and electrochemical characterization, J. Solid State Electrochem. 11 (2007) 887–898.
[51] S. Thiagarajan, R.-F. Yang, S.-M. Chen, Palladium nanoparticles modified electrode for the selective detection of catecholamine neurotransmitters in presence of ascorbic acid, Bioelectrochemistry 75 (2009) 163–169.
[52] K.H. Xue, C.X. Cai, H. Yang, Y.M. Zhou, S.G. Sun, S.P. Chen, G. Xu, Electrocatalysis and related factors of platinum microparticles dispersed on/in polypyrrole film in methanol oxidation, J. Power Sources 75 (1998) 207–213.
[53] F. Ficicioglu, F. Kadirgan, Electrooxidation of ethylene glycol on a platinum doped polyaniline electrode, J. Electroanal. Chem. 451 (1998) 95–99.
[54] İ. Becerik, S. Süzer, F. Kadirgan, Platinum–palladium loaded polypyrrole film electrodes for the electrooxidation of D-glucose in neutral media, J. Electroanal. Chem. 476 (1999) 171–176.
[55] E. Ticianelli, J.G. Beery, M.T. Paffet, S. Gottesfeld, An electrochemical, ellipsometric, and surface science investigation of the PtRu bulk alloy surface, J. Electroanal. Chem. 258 (1989) 61–77.
[56] A.F. Diaz, K.K. Kanazawa, in: J.S. Miller (Ed.), Extended Linear Chain Compounds, Plenum, New York, 1982.
[57] B.K. Jena, C.R. Raj, Morphology dependent electrocatalytic activity of Au nanoparticles, Electrochem. Commun. 10 (2008) 951–954.
[58] F. Ye, L. Chen, J.J. Li, J.L. Li, X. Wang, Shape-controlled fabrication of platinum electrocatalyst by pulse electrodeposition, Electrochem. Commun. 10 (2008) 476–479.
[59] X. Lin, Y. Zhang, W. Chen, P. Wu, Electrocatalytic oxidation and determination of dopamine in the presence of ascorbic acid and uric acid at a poly(p-nitrobenzenazo resorcinol) modified glassy carbon electrode, Sens. Actuators B: Chem. 122 (2007) 309–314.
[60] T. Yin, W. Wei, J. Zeng, Selective detection of dopamine in the presence of ascorbic acid by use of glassy-carbon electrodes modified with both polyaniline film and multi-walled carbon nanotubes with incorporated β-cyclodextrin, Anal. Bioanal. Chem. 386 (2006) 2087–2094.
[61] G. Jin, Y. Zhang, W. Cheng, Poly(p-aminobenzene sulfonic acid)-modified glassy carbon electrode for simultaneous detection of dopamine and ascorbic acid, Sens. Actuators B: Chem. 107 (2005) 528–534.
[62] D.R. Lide (Ed.), Handbook of Chemistry and Physics, 84th edition, CRC Press, 2004.
[63] C.R. Raj, K. Tokuda, T. Ohsaka, Electroanalytical applications of cationic self-assembled monolayers: square-wave voltammetric determination of dopamine and ascorbate, Bioelectrochemistry 53 (2001) 183–191.
[64] Z.D. Peterson, D.C. Collins, C.R. Bowerbank, M.L. Lee, S.W. Graves, Determination of catecholamines and metanephrines in urine by capillary electrophoresis–electrospray ionization–time-of-flight mass spectrometry, J. Chromatogr. B 776 (2002) 221–229.
[65] Đ. Ćulafić, V. Đukić, D. Mirković, A. Karamarković, Hyperdynamic circulation and serotonin levels in patients with liver cirrhosis, Jugoslov. Med. Biohem. 23 (2004) 31–35.
[66] Q. Yang, P. Atanasov, E. Wilkins, Development of needle-type glucose sensor with high selectivity, Sens. Actuators B: Chem. 46 (1998) 249–256.
[67] R.N. Goyal, V.K. Gupta, M. Oyama, N. Bachheti, Gold nanoparticles modified indium tin oxide electrode for the simultaneous determination of dopamine and serotonin: application in pharmaceutical formulations and biological fluids, Talanta 72 (2007) 976–983.

[68] S. Prakash, C.R.K. Rao, M. Vijayan, Polyaniline–polyelectrolyte–gold(0) ternary nanocomposites: synthesis and electrochemical properties, Electrochim. Acta 54 (2009) 5919–5927.

[69] W. Yan, X. Feng, X. Chen, X. Li, J.-J. Zhu, A selective dopamine biosensor based on AgCl–polyaniline core–shell nanocomposites, Bioelectrochemistry 72 (2008) 21–27.

[70] S. Thiagarajan, S.-M. Chen, Preparation and characterization of PtAu hybrid film modified electrodes and their use in simultaneous determination of dopamine, ascorbic acid and uric acid, Talanta 74 (2007) 212–222.

[71] L. Zhang, X. Jiang, Attachment of gold nanoparticles to glassy carbon electrode and its application for the voltammetric resolution of ascorbic acid and dopamine, J. Electroanal. Chem. 583 (2005) 292–299.

[72] J. Tashkhourian, M.R. Hormozi Nezhad, J. Khodavesi, S. Javadi, Silver nanoparticles modified carbon nanotube paste electrode for simultaneous determination of dopamine and ascorbic acid, J. Electroanal. Chem. 633 (2009) 85–91.

Biographies

Nada F. Atta is currently an Associate Professor at the Department of Chemistry, Faculty of Science, University of Cairo, Egypt. She earned a Ph.D. degree from the University of Cincinnati, Ohio, USA. Current research interests are imprinted sol–gel materials, sensors and nanoparticle-modified surfaces for catalysis applications.

Maher F. El-Kady received his B.S. in 2004 with first class honors from the Chemistry Department, Cairo University. He received his M.S. degree in 2008 from the same institute where he works as a research and teaching assistant. His research focuses on developing new nanomaterials based on conducting polymer thin films and metal nanoparticles for sensor applications. Currently, he is a Ph.D. student at the University of California, Los Angeles.