Palladium nanoclusters-coated polyfuran as a novel sensor for catecholamine neurotransmitters and paracetamol

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

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

ARTICLE INFO

ABSTRACT

A promising electrochemical biosensor was developed by electrodeposition of palladium nanoclusters on polyfuran film modified platinum electrode. This biosensor electrode was used to determine some catecholamines, namely dopamine, epinephrine and norepinephrine, ascorbic acid and paracetamol. The method of formation of the polymer film and deposition of Pd particles plays a key role in the electroactivity of the resulting hybrid material. This sensor effectively resolved the overlapping anodic peaks of ascorbic acid (AA), dopamine (DA) and paracetamol (ACOP) into three well-defined voltammetric peaks in differential pulse voltammetry analysis. The detection limit of DA in the absence and presence of AA and ACOP are eventually the same which indicates that the oxidation processes of DA, AA and ACOP are independent and that the simultaneous measurements of the three analytes are possible without interference. The electrodeposition of Pd on polyfuran improved exceptionally the detection limit about four decades. Moreover, diffusion coefficient measurements confirmed the fast electron transfer kinetics of the electrochemical oxidation of the analyte molecules at the sensor/solution interface. It is very interesting to note that the electrocatalytic effect of PF/Pd composite has been increased to be sometimes 21 times that of the pristine PF which has been considered for a long time to be of low conductivity and attracted low attention as a result of the difficulty of its formation and poor conductivity.

1. Introduction

The discovery of electric conductivity of conjugated organic polymers has opened a novel and a very important field of modern materials science. In the past few years the class of poly(heteroaromatic) compounds has been the center of great interest because of the high electrical conductivity, chemical stability and satisfactory processability. Among these polymers, poly(pyrroles), poly(thiophenes) and their derivatives have been extensively investigated. However, poly(furan) (PF) has received less attention because of the difficulty of synthesis as the monomer has high oxidation potential [1,2]. Many authors have overcome this difficulty by changing the experimental conditions [3–24]. In addition, various composites [25–30], copolymers [31–33], and bipolymers [16,18] based on PF have also been prepared. A review summarizing previous work on PF has recently appeared [34]. In this review, PF synthesis methods and the nucleation mechanism; the electrochemical, structural, morphological, and magnetic properties of PF; thermal behavior; theoretical calculations on PF, as well as its applications were reported. However, to the best of our knowledge, modification of PF films with metal particles has not

been reported in literature. It is thus of great importance to examine with enthusiasm different factors relevant to the synergistic effect between this polymer and Pd particles. This is due to the possibility of combining the properties of polymers (processability, chemical stability, and magnetic properties) with those of metals (electrical conductivity, optical and magnetic properties) in a single material.

Catecholamines, for example epinephrine (E), norepinephrine (NE), and dopamine (DA), are widely distributed and are important neurotransmitters and hormones in mammalian species [35]. Thus detecting and determining the concentrations of catecholamines in the presence of interfering species is an important goal in electrochemical analysis. Much attention has been given to the design and development of novel materials coated on electrode surfaces with improved molecular recognition capabilities [36–39]. The determination of monoamine neurotransmitters have been carried out by using spectrophotometer [40], fluorescence [41], chemical luminescence [42], pseudopolarography [43], voltammetry [44], capillary electrophoresis [45]. High performance liquid chromatography (HPLC) with electrochemical detection is most often used for the analysis of catecholamines and their metabolites [46–48,35]. The detection of neurotransmitters and their metabolites by electrochemical methods have attracted great interests because of their simplicity, rapidness and high sensitivity, the ability of sensing neurotransmitters in living organisms and in vivo real time analysis [49]. However, electrochemical analysis on the

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

unmodified electrodes such as glassy carbon (GC), Pt, Au electrodes has limitations because of overlapping voltammetric peaks, high concentrations of ascorbate, uric acid (UA) in typical biological matrices [50,51]. Recently, attention has been paid to develop a new generation of modified electrodes involving monolayers, conducting polymers and nanoparticles able to solve efficiently the problems encountered in the conventional unmodified electrodes.

Acetaminophen or paracetamol (ACOP) is an antipyretic and analgesic drug widely used worldwide for the relief of mild to moderate pain associated with headache, backache, arthritis and postoperative pain. It is also used for the reduction of fevers of bacterial or viral origin [52]. So it is very important to establish a simple, fast, sensitive and accurate detection method for ACOP. Moreover, ACOP is likely to interfere with DA and ascorbic acid (AA) determination. To our knowledge, few reports were published for the simultaneous determination of AA, DA, and ACOP in mixtures [53]. Voltammetric pulse techniques have been established to be very sensitive in the detection of micromolar or even nanomolar amounts of dopamine [54,55]. Moreover, electrochemical methods such as differential pulse voltammetry (DPV) can be used for obtaining better resolved Voltammetric characteristics for mixture of components. We employed DPV to understand the interdependence in the electrochemical signals on the oxidation of AA, DA and ACOP in the mixture. Furthermore, DPV was used for the simultaneous determination of AA, DA and ACOP.

In this work, a novel sensor is introduced for the first time by polymerizing PF and further modifies its surface with Pd nanoclusters. The sensor is demonstrated useful for the sensitive determination of catecholamines, AA and ACOP in mixtures with exceptionally high selectivity and sensitivity. Several parameters including the diffusion coefficients of the polymer/nanocluster sensor were also determined.

2. Experimental

2.1. Chemicals and reagents

All chemicals were used as received without further purification. Furan, tetrabutyl ammonium hexafluorophosphate (Bu$_4$NPF$_6$), acetonitrile (HPLC grade), hydroquinone, catechol, dopamine, epinephrine, norepinephrine, methyl-L-DOPA, p-aminophenol, paracetamol, ascorbic acid, sulfuric acid, were supplied by Aldrich Chem. Co. (Milwaukee, WI. USA). Palladium (II) chloride (Scherimg Kaul Paum AG, Berlin, Germany) was 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. For the purpose of specimens' preparation for the scanning electron microscope, platinum wires were polished before usage as previously described. 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.

2.3. Electrodeposition of Pd particles

The electrodeposition of Pd particles on the polymer film has been reported in our previous work [56]. Briefly, a polymer film is prepared by either bulk electrolysis, BE, or cyclic voltammetry, CV, methods and washed with doubly distilled water. This was followed by the electrochemical deposition of Pd particles on the polymer film from a solution of 2.5 mM PdCl$_2$ in 0.1 M HClO$_4$ by applying a double potential step (BE) or cyclic voltammetric program (CV) to the polymer. The double potential step conditions are (E_i = −0.05 V, Δt_i = 30 s, E_f = +0.01 V, Δt_f = 300 s), the electrode formed in this way is indicated Pt/PF/Pd(BE). In the cyclic voltammetric (CV) method, on the other hand, the electrode is cycled between −0.25 and +0.65 V at a scan rate of 50 mV s^{-1} for 25 cycles and the electrode formed in this way is indicated Pt/PF/Pd(CV).

3. Results and discussion

3.1. Electrochemical polymerization of furan

Furan has attracted less attention than pyrrole, thiophene, etc., because of its high oxidation potential and low conductivity. Low electrical conductivities may be attributed to type of dopant anion, short conjugation lengths, as well as the ring-opening reactions, the degree of cross-linking, and defects in the lattice that results in different morphologies [34]. Furan was electro-polymerized from a monomer solution containing 0.05 M furan/0.05 M Bu$_4$NPF$_6$/acetonitrile. Repeated cyclic voltammetry, CV, and bulk electrolysis, BE, methods were used for the electrochemical formation of polyfuran (PF) film. In the BE method a potential of 2.6 V was applied to the working electrode for 30 s whereas in the CV method the working electrode was cycled between −0.1 and +2.6 V at a scan rate of 50 mV s^{-1} for 15 cycles. Fig. 1A shows the repeated cyclic voltammograms taken during the formation of PF film by CV method. In the first cycle, in which PF is deposited over a clean surface of Pt, a sharp peak is observed around 1.95 V which decreases sharply in the second cycle. Furthermore, another peak is observed around 2.45 V in the first cycle, the intensity of this peak decreases in the subsequent cycles. However, the intensity of the previous signals seems to decrease only slightly in the subsequent scans which represent the deposition of more PF layers on PF surface. The increase in the number of scans resulted in the formation of irregular and low conductivity PF films that was manifested in a decrease in the current [16,18]. In addition, Nessakh et al. suggested that anodic peak current of 2-methylfuran decreases rapidly during repetitive cyclic voltammograms and it stabilizes at a small value when the electrode surface is coated by an insulating film [8]. Fig. 1B reveals the charge–time and current–time relationships obtained during the electrodeposition of PF by BE method. The charge increases with time while the current time transient shows an exponential decay indicating film thickening. The current is highest at the start of the experiment, in which PF is deposited over Pt, and decreases as time elapses. Again, these results confirm the insulating nature of PF on subsequent formation and thickening of the film.

3.2. Electroactivity of polyfuran films prepared under different electrochemical conditions

PF films were formed on Pt electrodes using BE, Pt/PF(BE), and CV, Pt/PF(CV), conditions. The electrocatalytic activity of both electrodes was tested using the hydroquinone/benzoquinone (HQ/BQ) redox system. Cyclic voltammograms were obtained at Pt/PF(BE) (I) and Pt/PF(CV) (II) electrodes in 5 mM analyte/0.1 M H$_2$SO$_4$ and the results are summarized in Table 1. Results show that lower oxida-
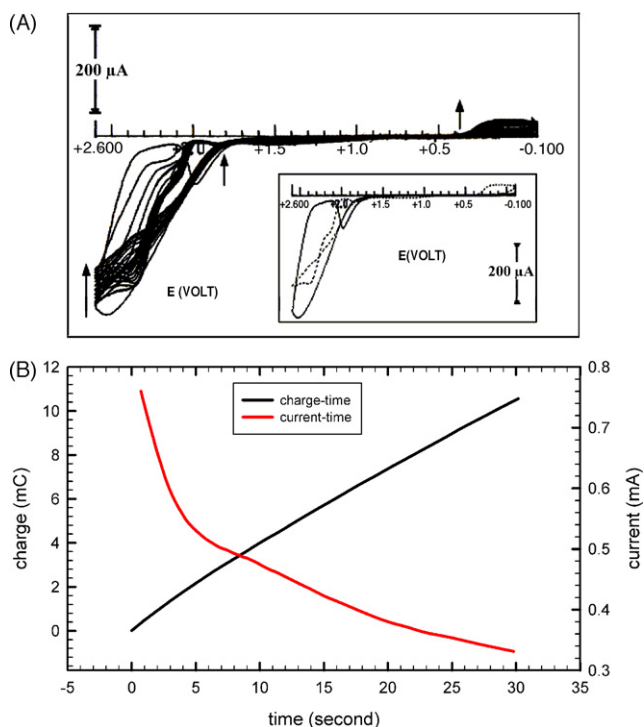
Fig. 1. Results for the electrodeposition of PF on Pt electrode from 0.05 M furan/0.05 M Bu₄NPF₆: (A) repeated cyclic voltammograms obtained during the formation of PF film on Pt electrode. $E_i = -0.1$ V, $E_f = +2.6$ V, number of cycles = 15, and scan rate = 50 mV s⁻¹. The inset: the first cycle, solid line, and the last cycle, dashed line, are only shown. (B) Bulk electrolysis results obtained during the formation of the polymer film at +2.6 V for 30 s.

Fig. 2. Scanning electron micrographs of (A) electrode I, scale bar = 50 μm, (B) electrode II, scale bar = 50 μm and (C) electrode I at a magnified scale, scale bar = 1 μm.

tion peak potential, E_{pa}, is observed at electrode (II) which indicates that the electro-oxidation of hydroquinone is thermodynamically more favorable at electrode (II) compared to electrode (I). Moreover, enhanced reversibility for the hydroquinone/benzoquinone redox system was observed at electrode (II) compared to electrode (I). This was indicated from the potential peak separation for this redox couple. Furthermore, lower oxidation peak current, I_{pa}, was observed at electrode (II). Therefore, the electro-oxidation of hydroquinone is kinetically less favorable at electrode (II) compared to electrode (I). However, the mechanism of the redox process did not change as indicated by the slopes of I–V curves prior the anodic and cathodic processes.

In addition, PF electrodes show lower electrocatalytic activity compared to bare Pt electrode. A comparison was made between Pt and PF modified Pt electrodes in terms of the anodic peak current values obtained from CV results for all the compounds studied. The current values and therefore electrocatalytic activities are always higher at Pt electrode compared to PF electrodes. Again, this indicates the slow charge transfer rate at the PF/solution interface.

Analysis of the surface morphology of these electrodes may explain this behavior. Fig. 2 shows the scanning electron micrographs for electrodes I and II. SEMs show a laminar structure for PF film in both cases. PF in electrode (I) is oriented at about 30° with respect to the longitudinal axis of the Pt electrode. On the other hand, laminar structure of PF in electrode (II) takes a different orientation. Hence, the angle of orientation changes by changing the method of polymerization. Magnification of the electrode (I) (Fig. 2C) shows that PF exists in two phases, amorphous and semi-crystalline, structures. This may be due to different simultaneous growth mechanisms for PF on Pt electrode. The first clear evidence for an ordered and porous PF/ClO₄⁻ morphology was presented by Carrillo et al. [11,34,57–59]. The film showed ordered nodular structure that was always oriented at 45° with respect to the longitudinal
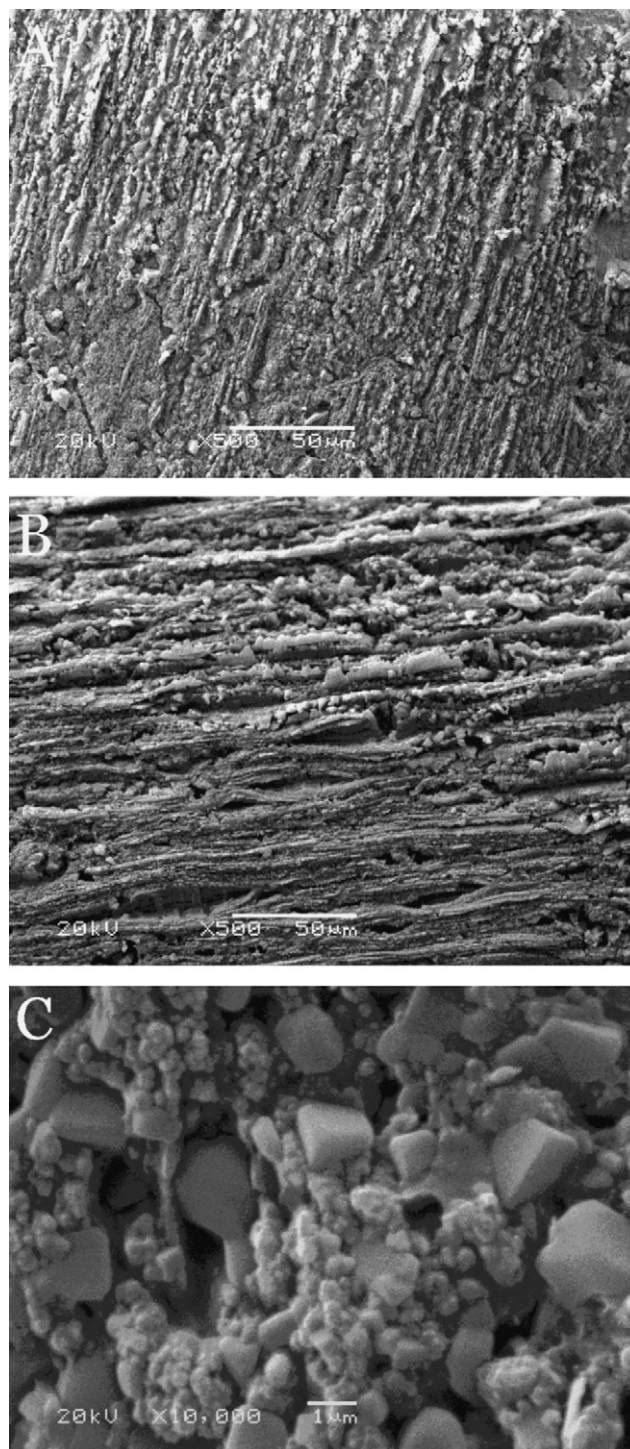
axis of the Pt electrode. The nodule area and the perimeter of the nodules were analyzed, from which it was established that their size diminished as the deposition potential increased [57]. The cross-section displays a porous texture composed of interlinked layers of nodules, with some cavities between the layers caused by non-simultaneous nucleation and by an alternative growth mechanism parallel to the electrode surface. A porous structure of polyfuran films was also found by Talu et al. [16,18] and Li et al. [60]. This laminar porous structure could account for the low values of the PF conductivity.

Table 1
Summary of the cyclic voltammetry results obtained at different electrodes in 5 mM analyte/0.1 M H_2SO_4.

Compound	Pt/PF				Pt/PF(BE)/Pd				
	BE[a]		CV[a]		BE[b]		CV[b]		
	E_{pa} (mV)	I_{pa} (μA)	E_{pa} (mV)	I_{pa} (μA)	E_{pa} (mV)	I_{pa} (μA)	E_{pa} (mV)	I_{pa} (μA)	Amount of current increased[c]
Hydroquinone	561	37.2	545	26.7	437	84.2	449	224.2	6.02
Catechol	654	44.9	635	35.3	542	95.7	553	266.6	5.92
Dopamine	635	15.2	604	12.0	533	141.1	546	285.4	18.75
Methyl-L-DOPA	650	9.2	623	9.1	551	67.2	566	196.3	21.01
Epinephrine	656	10.6	669	7.5	549	73.7	564	175.2	16.36
Norepinephrine	707	11.1	676	10.4	544	67.3	558	172.3	15.50
p-Aminophenol	575	9.82	550	10.9	541	82.2	558	183.7	18.63
Paracetamol	726	35.7	724	29.4	696	141.2	705	271.6	7.59
Ascorbic acid	522	10.6	577	7.47	296	69.4	305	124.5	11.70

[a] The method of formation of the polymer film.
[b] The method of deposition of Pd particles.
[c] The current at Pt/PF(BE)/Pd(CV) is normalized to the current at Pt/PF(BE).

3.3. Modification of PF with Pd particles

3.3.1. Effect of the method of polymerization of furan on the electrode response

It is necessary to test the influence of the method of formation of PF on the synergism between the polymer film and the subsequently loaded Pd particles. For this reason, Pt/PF(BE) (electrode I) or Pt/PF(CV) (electrode II) polymer films were prepared and Pd particles were then loaded by the cyclic voltammetry program (cf. Section 2.3). The resulting electrodes, Pt/PF(BE)/Pd(CV) (electrode III) or Pt/PF(CV)/Pd(CV) (electrode IV), were tested by CV in 5 mM hydroquinone/0.1 M H_2SO_4. The oxidation peak potential decreased largely as a result of the electrodeposition of Pd which indicates the thermodynamic feasibility of the redox reaction of HQ/BQ couple at the Pd modified PF electrodes compared to PF electrodes. It can also be noticed that the reversibility of the redox signals was enhanced considerably at Pd modified PF electrodes compared to PF electrodes. The catalytic effect of Pd particles on the kinetics of charge transfer can be manifested by comparing the peak current density for HQ oxidation at the PF and the PF/Pd electrodes. Thus, the anodic peak current at electrode (III) is about 6 times larger

compared to electrode (I), while it is only about 2.1 times larger at electrode (IV) compared to electrode (II). Thus, the redox reaction of dopamine is kinetically and thermodynamically more favorable at electrode (III) compared to other electrodes. Consequently, electrode (III) shows the most marked synergistic, electrocatalytic effect between PF film and Pd particles.

The variation of the electrocatalytic activity as a result of the method of polymer film formation can be assessed from the surface analysis of both electrodes. Fig. 3 shows scanning electron micrographs of electrodes (III) and (IV). The host polymer film show high roughness and some scattered pores with different sizes for the PF prepared by two different methods (Fig. 3a and b). This allows the chance for the deposition of Pd within the intercalation of the polymer layers which could result in an effective interaction between the polymer film and Pd particles. Thus, Pd starts to deposit from the interior of the polymer matrix and grow to the outside (cf. Fig. 3c and d). The strong interaction between PF and Pd particles and the high electrocatalytic activity of Pd modified PF electrodes compared to PF electrodes could be explained in terms of the small grain size of Pd (with nano-dimensions). It can also be noticed that Pd forms clusters in the micrometer range,
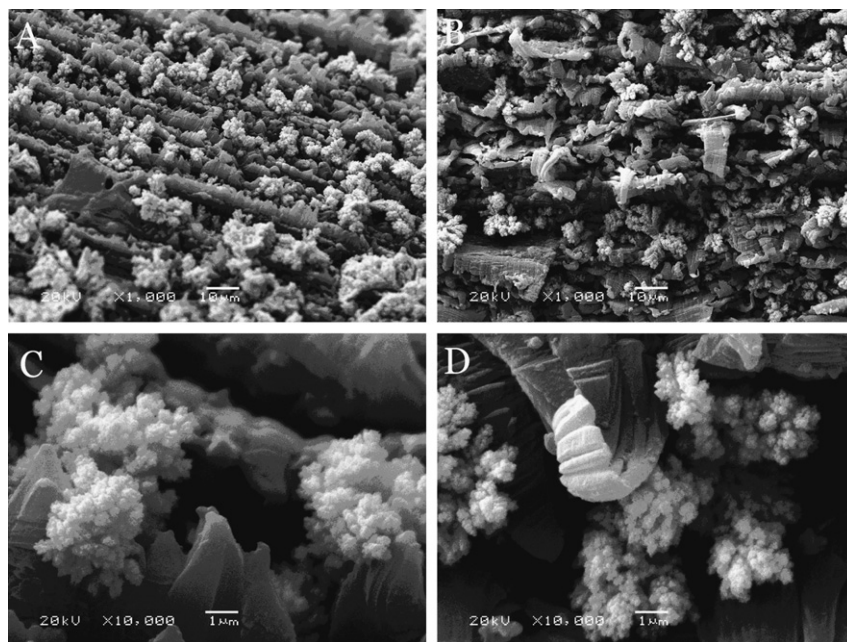

Fig. 3. Scanning electron micrographs of (a and c) Pt/PF(BE)/Pd(CV), electrode III (b and d) Pt/PF(CV)/Pd(CV), electrode IV. Scale bar (a and b) = 10 μm, (c and d) = 1 μm.

however, they are composed of smaller particles in the nanometer range.

3.3.2. Effect of the method of deposition of Pd particles on the electroactivity of PF electrodes

The effect of presence of Pd as well as the method of its deposition on the electroactivity of PF electrodes is considered here. At first, PF polymer film was prepared using BE conditions as it gives better synergistic effects on the current response of the electrode. Subsequently, Pd was deposited over the polymer film using the double potential step and the cyclic voltammetry methods (Section 2.3). The electroactivity of the resulting electrodes, namely, Pt/PF(BE)/Pd(BE) (electrode V) and Pt/PF(BE)/Pd(CV) (electrode III) were tested by cyclic voltammetry in 5 mM hydroquinone/0.1 M H$_2$SO$_4$. Analysis of these results again reveals that the redox reaction of the HQ/BQ redox couple is thermodynamically and kinetically more favorable at PF electrodes modified with Pd particles compared to the pristine PF electrodes. Moreover, incorporation of Pd into PF films results in enhanced reversibility of the redox reaction of the HQ/BQ system. The value of the potential peak separation is lowered by the deposition of Pd. In addition, the ratio of the anodic to the cathodic peak current (i_{pa}/i_{pc}) gets closer to unity by the deposition of Pd. The foregoing results confirm the reasonable reversibility of HQ/BQ system at electrode (III) [61,62]. Hence, electrode (III) has the best synergistic effect between the polymer film and Pd particles in terms of the thermodynamic and kinetic feasibility of the redox reaction.

In order to characterize the reproducibility of the modified electrode, repeated cyclic voltammetry (CV) experiment was run in 5 mM DA/0.1 M H$_2$SO$_4$. The relative standard deviation (R.S.D.) was about 3% after 50 successive CVs indicating that the designed sensor had an excellent reproducibility. On the other hand, electrode (I) showed a change of 26% of current values at oxidation peak potential from the second cycle which indicate very weak reproducibility. The plot of oxidation peak current versus the square root of scan rate yields a straight line for electrode (III) in the range of 10–200 mV s^{-1}. This suggests that the oxidation of dopamine at electrode (III) is diffusion controlled.

3.4. Cyclic voltammetry results for the studied compounds at Pd modified PMPy electrodes

Table 1 shows the results of the cyclic voltammograms of the studied compounds at electrodes I, II, III and V. It can be noticed that all compounds show a sluggish and much smaller CV peak response with high oxidation potentials at electrodes I, II. On the other hand, electrodes III, V showed a negative shift in the oxidation overpotential and increase in both redox peak currents with more reversible behavior. The current increase at Pd modified PF electrode (electrode III) is sometimes 21 times larger compared to the pristine PF electrode (electrode I). The decrease of the oxidation peak potential and the increase of the peak current prove the excellent electrocatalytic effect of Pd particles imparted to electrodes III and V. Furthermore, the redox processes turn to be more reversible, suggesting that Pd particles accelerate the electron transfer of the studied compounds at the electrode/solution interface. Cyclic voltammograms for two compounds of biological and pharmaceutical interest are shown, Fig. 4. A remarkable enhancement in the current response followed by a drop in peak potential provide 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. Stability of the electrochemical redox signal is also of importance for a superior electrode. The cyclic voltammetric signal at the Pd modified electrodes for all compounds exhibits excellent stability by repetition for up to 50 cycles.
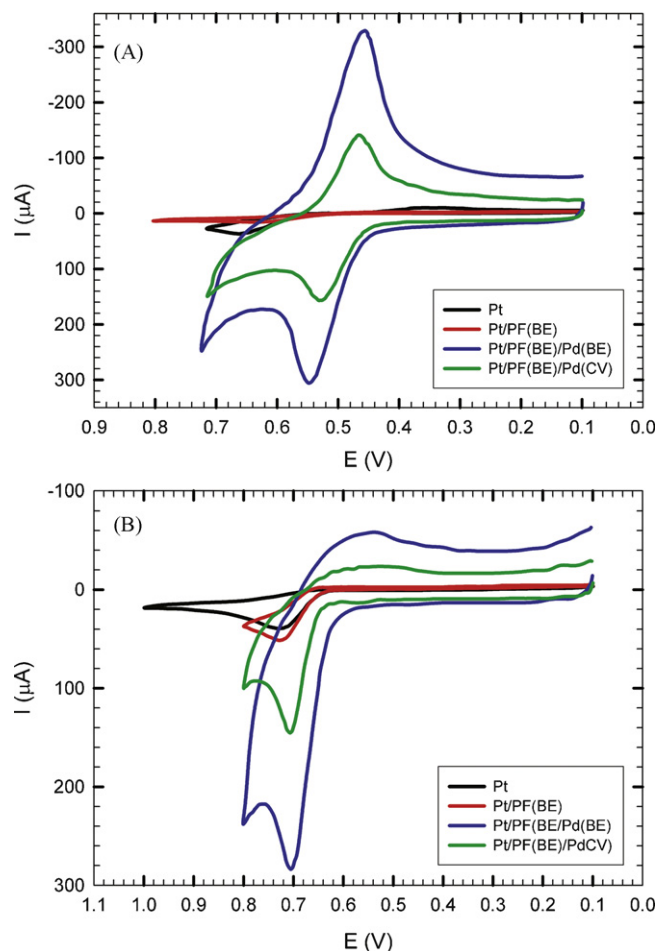

Fig. 4. cyclic voltammograms obtained for (a) 5 mM DA (b) 5 mM ACOP at different electrodes.

3.5. Apparent diffusion coefficients of the studied compounds at different electrodes

The dependence of the anodic peak current density on the scan rate has been used for the estimation of the "apparent" diffusion coefficient, D_{app}, for the compounds studied. D_{app} values were calculated from Randles Sevcik equation [63].

$$i_p = 2.69 \times 10^5 n^{3/2} A C^0 D^{1/2} v^{1/2}$$

where i_p is the peak current density (A cm^{-2}), n is the number of electrons transferred at $T = 298$ K, A is the geometrical electrode area (0.0176 cm^2), C^0 is the analyte concentration (5×10^{-6} mol cm^{-3}), D is the diffusion coefficient of the electroactive species (cm^2 s^{-1}), and v is the scan rate (V s^{-1}). It is important to notice that the apparent surface area used in the calculations did not take into account the surface roughness, which is an inherent characteristic for all polymer films formed using the electrochemical techniques. D_{app} values are between 10^{-4} and 10^{-8} cm^2 s^{-1} (Fig. 5). The electrodeposition of Pd affects remarkably the diffusion component of the charge transfer at the electrode surface as indicated by the D_{app} values. Sometimes, the increase in D_{app} values is about four decades that can only be explained in terms of the exceptional catalytic role played by the Pd particles. This is possibly due to quick mass transfer of the analyte molecules towards electrode surface from bulk solutions and/or fast electron transfer process of electrochemical oxidation of the analyte molecule at the interface of the electrode surface and the solutions [64,65]. These results are consistent with recent publications [66,67]. Furthermore, D_{app}
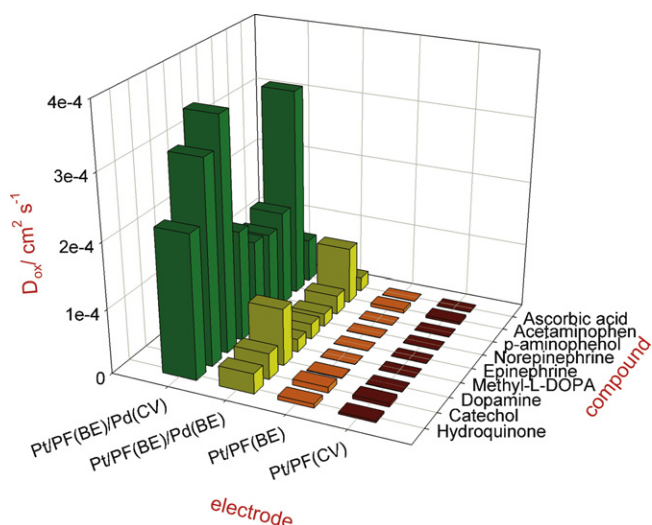
Fig. 5. Apparent diffusion coefficient values for all studied compounds as calculated from the oxidation segment of the corresponding CVs at: Pt/PF(BE), Pt/PF(CV), Pt/PF(BE)/Pd(BE), and Pt/PF(BE)/Pd(CV) electrodes.

values increase in the following order: electrode (II) < electrode (I) < electrode (V) < electrode (III) which is in consistence with the cyclic voltammetric results.

3.6. pH study

The effect of solution pH on the electrocatalytic oxidation of DA at the Pt/PF(BE)/Pd(CV) modified electrode was studied by CV in 0.1 M PBS with the pH range of 2–11, Fig. 6. It was found that both the anodic and the cathodic peak potentials shifted negatively with the increase of solution pH, indicating that the electrocatalytic oxidation of DA at the Pt/PF(BE)/Pd(CV) modified electrode is a pH-dependent reaction. The relationship between the anodic peak potential and the solution pH value (over the pH range from 2 to 7) could be fit to the linear regression equation of E_{pa} (V) = 0.6439 − 0.0613 pH, with a correlation coefficient of r^2 = 0.9997. The slope was found to be −61.3 mV/pH unit over the pH range from 2 to 7, which is very close to the theoretical value of −59 mV. This indicates that the number of protons and electrons involved in the oxidation mechanism is equal [68]. As the dopamine oxidation is a two-electron process, the number of protons involved
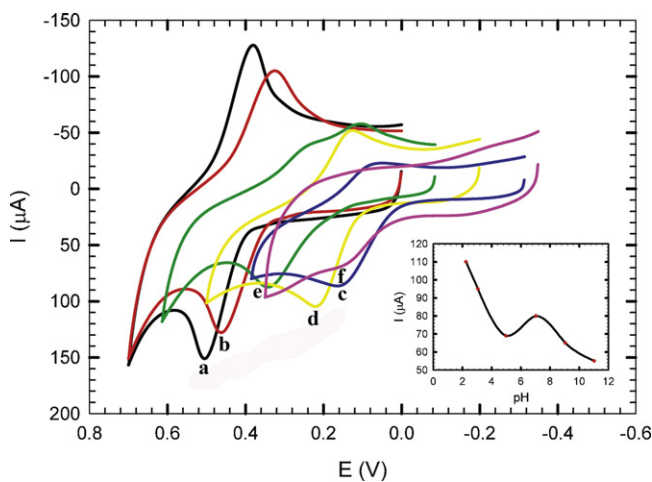

Fig. 6. Cyclic voltammetric response of the Pt/PF(BE)/Pd(CV) electrode to 5 mM DA in 0.1 M PBS of different pH values: (a) pH 2.2, (b) pH 3, (c) pH 5, (d) pH 7, (e) pH 9, (f) pH 11. Scan rate 50 mV s^{-1}. Inset: plot of the anodic peak current versus pH value.
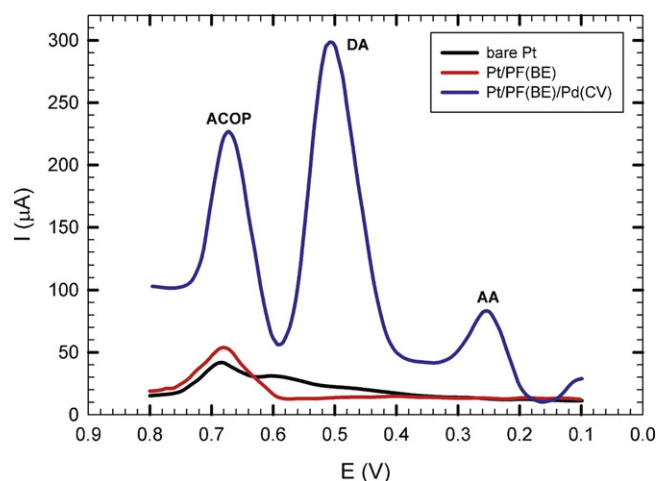

Fig. 7. Differential pulse voltammograms, DPVs, obtained at bare Pt, Pt/PF(BE) (electrode I) and Pt/PF(BE)/Pd(CV) (electrode III) for a tertiary mixture of 5 mM AA + 5 mM DA + 5 mM ACOP in 0.1 M H$_2$SO$_4$. DPV conditions: Pulse amplitude = 50 mV, scan rate = 20 mV s^{-1}, sample width = 17 ms, pulse width = 50 ms, pulse period = 200 ms, and quiet time = 2 s.

is also predicted to be two. In solution, the pK_a's of dopamine are 8.9 (pK_{a1}) and 10.6 (pK_{a2}) [69]. A linear behavior was observed for pH values in the range from 2 to 7 and just a little deviation was obtained at pH 9. This indicates the deprotonation of dopamine at pH 9 so that it is no longer a two-proton, two-electron process at this point and other equilibria should be taken into account. At pH 11 the redox reaction of DA is no longer pH dependent as dopamine is completely deprotonated at this pH. The peak current (Fig. 6, inset) decreased from pH 2 to 5 then increased up to pH 7. Above pH 7, the peak current decreased again.

3.7. Interference study

3.7.1. Voltammetric response of DA, ACOP, and AA in their mixture

Sensitivity and selectivity of electrode (III) for the simultaneous determination of AA, DA and ACOP were evaluated for a mixture of AA, DA and ACOP at electrode (III). Fig. 7 shows the Differential pulse voltammograms, DPVs, recorded for a mixture of AA (5 mM), DA (5 mM) and ACOP (5 mM) at bare Pt and electrodes (I) and (III) in 0.1 M H$_2$SO$_4$. We can see that bare Pt and electrode (I) cannot separate the voltammetric signals of AA, DA and ACOP. Therefore it is difficult to use bare Pt and electrode (I) for the voltammetric determination of this ternary mixture. On the other hand, electrode (III) resolved the mixed voltammetric signals into three well-defined voltammetric peaks at 246, 508 and 673 mV corresponding to the oxidation of AA, DA and ACOP, respectively. The parameters used during the DPV are set to be as follows: pulse width (50 ms), pulse period (200 ms) and pulse amplitude (10 mV). Generally, for a given concentration of DA, a comparatively large oxidation current was noticed in the presence of AA at conventional electrodes. 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 [70,51]. Therefore, determination of concentration of DA could not be achieved accurately in the presence of AA. However, in the present work, AA is readily oxidized at the new sensor surface well before the oxidation potential of DA is reached. Hence, in addition to the wider potential difference (262 mV) for the oxidation of AA and DA at electrode (III), the interference from oxidation product of DA is minimized. Thus, the combined presence of PF and Pd nanoparticles in electrode (III) is advantageous in the simultaneous determination of AA, DA and ACOP.
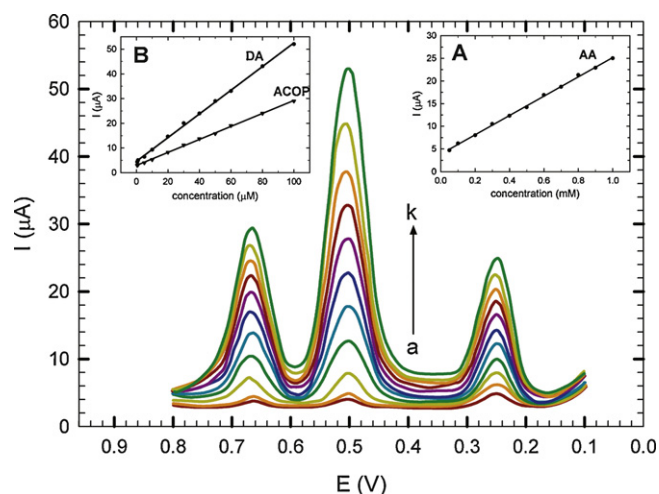
Fig. 8. DPV curves of DA, ACOP and AA at electrode (III) in 0.1 M H$_2$SO$_4$. Concentrations of the three compounds (a–k): AA: 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 mM, DA and ACOP: 0.5, 1, 5, 10, 20, 30, 40, 50, 60, 80, 100 μM. Insets: the corresponding calibration curves for (a) AA, (b) DA and ACOP.

3.7.2. Simultaneous determination of DA, ACOP at high concentrations of AA

In biological environments, the concentration of AA is large compared to DA. So it is important to investigate the electrochemical response of DA and ACOP in the presence of large concentrations of AA. DPV experiments were performed at electrode (III) (Fig. 8) while changing the concentration of DA and ACOP simultaneously at the micromolar levels and AA at the millimolar level. The peak current values were proportional to the concentrations of DA, ACOP and AA in the mixture. The oxidation current of AA increases linearly with its concentration between 0.05 and 1.0 mM (inset of Fig. 8). For the regression plot of peak current versus AA concentration, the slope is 21.31 μA mM^{-1} and correlation (r^2) is 0.9986. At the same time, the calibration plots of both DA and ACOP are linear between 0.5 and 100 μM with slopes of 0.4784 μA μM^{-1} (DA), 0.2637 μA μM^{-1} (ACOP) and correlations of 0.9990 (DA), 0.9993 (ACOP). The detection limits (S/N = 3) are 7.13 × 10^{-6}, 4.82 × 10^{-8} and 7.64 × 10^{-8} M for AA, DA and ACOP, respectively. The separations of peaks between either two-peak potentials were large enough to determine DA and ACOP individually and simultaneously in the presence of high concentration of AA. Hence, it is confirmed that for the oxidation of AA, DA or ACOP at electrode (III), the other components do not give any interference to the electrochemical signal. Interestingly, the difference between peak potentials does not change with concentration of AA and DA in the mixture. To our knowledge, only one report was published for the analysis of AA, DA, and ACOP mixture [53]. In this report the detection limits were 4.1 × 10^{-8}, 1.2 × 10^{-6} and 2.3 × 10^{-6} M for AA, DA and ACOP, respectively. The latter values were achieved at carbon-coated nickel magnetic nanoparticles modified glassy carbon electrodes (C–Ni/GCE). When compared to our results, lower detection limits have been achieved at Pt/PF(BE)/Pd(CV) electrode.

It is very interesting to note that the detection limit of DA (S/N = 3) at electrode (III) in the absence and presence of AA and ACOP are eventually the same (i.e. 5.36 × 10^{-8} and 4.82 × 10^{-8} M, respectively), which indicates that the oxidation processes of DA, AA and ACOP at electrode (III) are independent and that the simultaneous or independent measurements of the three analytes are possible without interference. Furthermore, the detection limit of DA at electrode (I) was only 2.15 × 10^{-4} M. Thus, the electrodeposition of Pd on polyfuran made an enhancement for the detection limit of about four decades which is an excellent result for these types of polymers. It is important to mention that with the use of

"small current" electrical transducers it will be possible to measure small currents to allow the detection of pico-mole concentrations for each of DA and ACOP simultaneously in presence of relatively high concentrations of AA.

The other main interferences were examined and it was found that 1.0 mM glucose, 1.0 mM uric acid did not interfere with 100 μM DA and ACOP oxidation.

4. Conclusions

This study has indicated that the Pd modified PF composite electrode exhibits highly electrocatalytic activity to the oxidation of catecholamines, some organic compounds, ascorbic acid and paracetamol. The methods of deposition of the polymer film and Pd particles were found to be key factors in controlling the electroactivity of this hybrid electrode. In addition, it has been shown that this composite has good stability, reproducibility, selectivity and sensitivity. It is very interesting to note that the electrocatalytic power of PF/Pd composite has been increased to be sometimes 21 times that of the pristine PF which has been considered for a long time to be of low conductivity and attracted low attention as a result of the difficulty of its formation. Ascorbic acid, dopamine and paracetamol coexisting in a homogeneous solution can be simultaneously determined at this modified electrode. The separations of peaks were large enough to determine DA and ACOP individually and simultaneously in the presence of high concentration of AA without any interference. The detection limits (S/N = 3) are 7.13 × 10^{-6}, 4.82 × 10^{-8} and 7.64 × 10^{-8} M for AA, DA and ACOP, respectively.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.snb.2009.07.002.

References

[1] E.T. Kang, K.G. Neoh, Halogen induced polymerization of furan, Eur. Polym. J. 23 (9) (1987) 719–722.
[2] V. Hernandez, F.J. Ramirez, G. Zotti, J.T. Lopez Navomete, Resonance Raman and FTIR spectra of pristine and doped polyconjugated polyfuran, Chem. Phys. Lett. 191 (5) (1992) 419–422.
[3] G. Tourillon, F. Garnier, New electrochemically generated organic conducting polymers, J. Electroanal. Chem. 135 (1) (1982) 173–178.
[4] S. Pons, A. Scott Hinman, Anodic oxidation of furans in aprotic solvents, Electrochim. Acta 29 (9) (1984) 1251–1255.
[5] F. Tediar, Électropolymérisation du furanne, 1. Obtention des produits sur différents substrats, Eur. Polym. J. 21 (3) (1985) 317–319.
[6] H.S. Nalwa, Phase transitions in polypyrrole and polythiophene conducting polymers demonstrated by magnetic susceptibility measurements, Phys. Rev. B. 39 (9) (1989) 5964–5974.
[7] G. Zotti, G. Schiavon, N. Comisso, A. Berlin, G. Pagani, Electrochemical synthesis and characterization of polyconjugated polyfuran, Synth. Met. 36 (3) (1990) 337–351.
[8] B. Nessakh, Z. Kotkowska-Machnik, F.J. Tedjar, Electrochemical behaviour of furan, 2-methylfuran and 2,5-dimethylfuran in acetonitrile, J. Electroanal. Chem. 296 (1) (1990) 263–268.
[9] G. Troch-Nagels, R. Winand, A. Weymeersch, L. Renard, Electron conducting organic coating of mild steel by electropolymerization, J. Appl. Electrochem. 22 (1992) 756–764.
[10] S. Glenis, M. Benz, E. LeGoff, J.L. Schindler, C.R. Kannewurf, M.G. Kanatzidis, On polyfuran: a new synthetic approach and electronic properties, J. Am. Chem. Soc. 115 (1993) 12519–12525.
[11] M.J. González-Tejera, I. Carrillo, I. Hernández-Fuentes, Influence of the electropolymerization parameters on the generation of polyfurane perchlorate doped films, Synth. Met. 92 (1998) 187–195.

[12] M.J. González-Tejera, I. Carrillo, Cyclic voltammetric behaviour of polyfuran perchlorate doped films, J. Appl. Electrochem. 32 (4) (2002) 447–453.
[13] B. Demirboğa, A.M. Önal, Electrochemical polymerization of furan and 2-methylfuran, Synth. Met. 99 (3) (1999) 237–242.
[14] X. Wan, F. Yan, S. Jin, X. Liu, G. Xue, Low potential electrochemical synthesis of polyfuran and characterization of the obtained free-standing film, Chem. Mater. 11 (1999) 2400–2407.
[15] X.-B. Wan, L. Li, J.-B. He, D.-S. Zhou, G. Xue, T.-W. Wang, Electrochemical degradation of polyfuran in wet acetonitrile and aqueous solutions, J. Appl. Polym. Sci. 86 (2002) 3160–3165.
[16] M. Talu, M. Kabasakolğlu, F. Yildirim, B. Sari, Electrochemical synthesis and characterization of homopolymers of polyfuran and polythiophene and bipolymer films polyfuran/polythiophene and polythiophene/polyfuran, Appl. Surf. Sci. 181 (2001) 51–60.
[17] I. Carrillo, E. Sánchez de la Blanca, M.J. González-Tejera, Influence of the electropolymerisation time on the nucleation mechanism, structure and morphology of polyfurane/perchlorate doped films, Polymer 42 (2001) 9447–9453.
[18] M. Kabasakaloğlu, M. Talu, F. Yildirim, B. Sari, The electrochemical homopolymerization of furan and thiophene and the structural elucidation of their bipolymer films, Appl. Surf. Sci. 218 (2003) 85–97.
[19] C. Liu, J. Zhang, G. Shi, Y. Zhao, Raman spectra of electrosynthesized polyfuran: a combined experimental and theoretical study, J. Phys. Chem. 108 (2004) 2195–2199.
[20] T. Ogawa, T. Igarashi, T. Kawanishi, T. Kitamura, K. Hoshino, Dinitrogen fixation using polyfuran-titanium oxide and polycarbazole-titanium oxide hybrid junction systems, J. Photopolym. Sci. Technol. 17 (2004) 143–148.
[21] M.A. del Valle, L. Ugalde, F.R. Diaz, M.E. Bodini, J.C. Bernède, Effect of working conditions on the morphology of electrosynthesized polyfuran, J. Appl. Polym. Sci. 92 (2) (2004) 1346–1354.
[22] M.A. del Valle, L. Ugalde, F. Pino, F.R. Diaz, J.C. Bernède, Nucleation and growth mechanisms of poly (furan). Effect of electrolyte and monomer concentration in acetonitrile, J. Braz. Chem. Soc. 15 (2) (2004) 272–276.
[23] S. Tirkes, A.M. Önal, Electrosynthesis of polyfuran in acetonitrile-boron trifluoride-ethyl ether mixture and its device application, J. Appl. Polym. Sci. 103 (2) (2007) 871–876.
[24] K. Imanishi, M. Satoh, Y. Yasuda, R. Tsushima, S. Aoki, Solvent effect on electrochemical polymerization of aromatic compounds, J. Electroanal. Chem. 242 (1–2) (1988) 203–208.
[25] A. Gök, B. Sari, M. Talu, Synthesis and characterization of novel polyfuran/poly (2-iodoaniline) conducting composite, J. Appl. Polym. Sci. 89 (2003) 2823–2830.
[26] A. Gök, B. Sari, M. Talu, Chemical preparation of conducting polyfuran/poly (2-chloroaniline) composites and their properties: a comparison of their components, polyfuran and poly (2-chloroaniline), J. Appl. Polym. Sci. 88 (13) (2003) 2924–2931.
[27] A. Gök, B. Sari, M. Talu, Preparation and characterization of polyfuran/poly (2-fluoroaniline) conducting composites, J. Polym. Sci. B: Polym. Phys. 42 (2004) 3359–3367.
[28] A. Gök, B. Sari, M. Talu, Polymers, composites, and characterization of conducting polyfuran and poly (2-bromoaniline), J. Appl. Polym. Sci. 98 (2005) 2048–2057.
[29] N. Ballav, M. Biswas, Preparation and evaluation of nanocomposites of polyfuran with Al$_2$O$_3$ and montmorillonite clay, Polym. Int. 53 (2004) 1467–1472.
[30] N. Ballav, M. Biswas, Conducting composites of polythiophene and polyfuran with acetylene black, Polym. Int. 54 (4) (2005) 725–729.
[31] X. Wan, W. Zhang, S. Jin, G. Xue, Q.-D. You, B. Che, The electrochemical copolymerization of pyrrole and furan in a novel binary solvent system, J. Electroanal. Chem. 470 (1999) 23–30.
[32] L. Li, W. Chen, N. Xu, Z. Xiao, G. Xue, Electrochemical copolymerization of furan and 3-methyl thiophene, J. Mater. Sci. 39 (2004) 2395–2398.
[33] R.M. McConnell, W.E. Godwin, S.E. Baker, K. Powell, M. Baskett, A. Morara, Polyfuran and co-polymers: a chemical synthesis, Int. J. Polym. Mater. 53 (2004) 697–708.
[34] M.J. González-Tejera, E. Sánchez de la Blanca, I. Carrillo, Polyfuran conducting polymers: synthesis, properties, and applications, Synth. Met. 158 (2008) 165–189.
[35] M. Tsunoda, Recent advances in methods for the analysis of catecholamines and their metabolites, Anal. Bioanal. Chem. 386 (2006) 506–514.
[36] A. Malinauskas, Electrocatalysis at conducting polymers, Synth. Met. 107 (1999) 75–83.
[37] M. Gerard, A. Chaubey, B.D. Malhotra, Application of conducting polymers to biosensors, Biosens. Bioelectron. 17 (2002) 345–359.
[38] B. Adhikari, S. Majumdar, Polymer in sensor applications, Prog. Polym. Sci. 29 (2004) 699–766.
[39] A. Ramanavicius, A. Ramanaviciene, A. Malinauskas, Electrochemical sensors based on conducting polymer—polypyrrole, Electrochim. Acta 51 (27) (2006) 6025–6037.
[40] P.B. Issopoulos, S.E. Salta, High-sensitivity microdetermination of sub-micromolar concentrations of levodopa, carbidopa and α-methyldopa using a coupled redox-complexation reaction, II, Farmaco 51 (1996) 673–678.
[41] H. Nohta, T. Yukizawa, Y. Ohkura, M. Yoshimura, J. Ishida, M. Yamaguchi, Aromatic glycinonitriles and methylamines as pre-column fluorescence derivatization reagents for catecholamines, Anal. Chim. Acta 344 (1997) 233–240.
[42] N.W. Barnett, B.J. Hindson, S.W. Lewis, Determination of 5-hydroxytryptamine (serotonin) and related indoles by flow injection analysis with acidic potassium permanganate chemiluminescence detection, Anal. Chim. Acta 362 (1998) 131–139.
[43] Y. Wu, R. Fan, J. Di, Electrochemical study of electron transfer between dopamine and ferrocene at liquid/liquid interface, Chin. J. Anal. Chem. 24 (1996) 873–876.
[44] 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.
[45] W. Jin, L.T. Jin, G.S. Shi, J.N. Ye, Determination of monoamine transmitters and their metabolites by capillary electrophoresis with electrochemical detection, Anal. Chim. Acta 382 (1999) 33–37.
[46] 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.
[47] W. Zhang, F. Wan, J. Gu, S. Ai, J. Ye, K. Yamamoto, L. Jin, In vivo determination of tetrahydrobiop- terin 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.
[48] A. Bose, S.C. Durgbanshi, M.G. Broch, M. Agustí, J. Peiró, Romero, Direct Injection analysis of epinephrine, norepinephrine, and their naturally occurring derivatives in serum by micellar liquid chromatography with electrochemical detection, J. Liq. Chromatogr. Related Technol. 28 (2005) 3265–3281.
[49] B.J. Venton, R.M. Wightman, Psychoanalytical electrochemistry: dopamine and behavior, Anal. Chem. 75 (2003) 414A–421A.
[50] J. Chen, C.S. Cha, J. Electroanal. Chem. 463 (1999) 93.
[51] M.A. Dayton, A.G. Ewing, R.M. Wightman, Response of microvoltammetric electrodes to homogeneous catalytic and slow heterogeneous charge transfer reactions, Anal. Chem. 52 (1980) 2392–2396.
[52] M. Boopathi, M.S. Won, Y.B. Shim, A sensor for acetaminophen in a blood medium using a Cu (II)-conducting polymer complex modified electrode, Anal. Chim. Acta 512 (2004) 191–197.
[53] S.-F. Wang, F. Xie, R.-F. Hu, Carbon-coated nickel magnetic nanoparticles modified electrodes as a sensor for determination of acetaminophen, Sens. Actuators B 123 (2007) 495–500.
[54] K. Wu, S. Hu, J. Fei, W. Bai, Mercury-free simultaneous determination of cadmium and lead at a glassy carbon electrode modified with multi-wall carbon nanotubes, Anal. Chim. Acta 489 (2003) 215–221.
[55] S. Senthil Kumar, J. Mathiyarasu, K. LakshminarasimhaPhani, Exploration of synergism between a polymer matrix and gold nanoparticles for selective determination of dopamine, J. Electroanal. Chem. 578 (2005) 95–103.
[56] 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.
[57] I. Carrillo, M.J. Gonzalez-Tejera, I. Hernandez-Fuentes, C. Barba, Morphology of polyfuran perchlorate doped films by scanning electron microscopy, Solid State Commun. 95 (2) (1995) 107–110.
[58] I. Carrillo, C. Barba, M.J. Gonzalez-Tejera, I. Hernandez-Fuentes, Microstructure of polyfuran/perchlorate-doped films by scanning and transmission electron microscopies and electron-diffraction, Macromolecules 29 (17) (1996) 5585–5589.
[59] I.C. Ramiro, M.J. Gonzalez-Tejera, Influence of synthesis conditions on the morphology of perchlorate doped polyfuran films, Polym. Int. 49 (2000) 1565–1571.
[60] L. Li, X. Wan, G. Xue, Impedance characteristics of polyfuran films, Chin. J. Polym. Sci. 20 (2002) 419–423.
[61] A.J. Bard, L.R. Faulkner, Electrochemical Methods, Fundamentals and Applications, 2nd ed., John Wiley & Sons, New York, 2001.
[62] A.P. Brown, F.C. Anson, Cyclic and differential pulse voltammetric behaviour of reactants confined to electrode surface, Anal. Chem. 49 (1977) 1589–1595.
[63] P.T. Kissinger, W.R. Heineman (Eds.), Laboratory Techniques in Electroanalytical Chemistry, Marcel Dekker, New York, 1984, p. 82.
[64] Q. Wan, N. Yang, X. Zou, H. Zhang, B. Xu, Voltammetric behavior of vitamin B$_2$ on the gold electrode modified with a self-assembled monolayer of L-cysteine and its application for the determination of vitamin B$_2$ using linear sweep stripping voltammetry, Talanta 55 (2002) 459–467.
[65] V.S. Vasantha, S.-M. Chen, Electrocatalysis and simultaneous detection of dopamine adn ascorbic acid using poly (3,4-ethylenedioxy)thiophene film modified electrodes, J. Electroanal. Chem. 592 (2006) 77–87.
[66] M. Hasik, E. Wenda, C. Paluszkiewicz, A. Bernasik, J. Camra, Poly (o-methoxyaniline)-palladium systems: effect of preparation conditions on physico-chemical properties, Synth. Met. 143 (2004) 341–350.
[67] F. Ye, J. Nan, L. Wang, Y. Song, K.-B. Kim, The ultrasonic electropolymerization of an 5-[o-(4-bromine amyloxy)phenyl]-10,15,20-triphenylporphrin (o-BrPETPP) film electrode and its electrocatalytica properties to dopamine oxidation in aqueous solution, Electrochim. Acta 53 (2008) 4156–4160.
[68] X. Jiang, X. Lin, Overoxidized polypyrrole film directed DNA immobilization for construction of electrochemical micro-biosensors and simultaneous determination of serotonin and dopamine, Anal. Chim. Acta 537 (2005) 145–151.
[69] D.R. Lide (Ed.), Handbook of Chemistry and Physics, 84th edition, CRC Press, 2004.
[70] 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.

Biographies

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

Maher F. El-Kady received his B.S. in 2004 with first class honors from 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 focus 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.

Ahmed Galal is Professor of Chemistry at the Department of Chemistry, Faculty of Science, University of Cairo. He holds a PhD degree from the University of Cincinnati. Research work of Dr. Galal is in the area of new and advanced materials with emphasis on nano-structured materials. Other interests are molecular recognition, sensors and conducting polymers.