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SCIENCE DIRECT®

Talanta 66 (2005) 111–117

Talanta

www.elsevier.com/locate/talanta

Electrosynthesis and analytical performances of functionalized poly (pyrrole/β-cyclodextrin) films

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Received 13 April 2004; received in revised form 9 September 2004; accepted 14 October 2004
Available online 25 November 2004

Abstract

The supramolecular complexing properties of cyclodextrins (CDs) have been investigated inside a conducting polymer environment. In this work, we report the synthesis and characterization of a polypyrrole/β-cyclodextrin (Ppy/β-CD) film at a glassy carbon (GC) electrode surface. The polypyrrole/β-cyclodextrin (Ppy/β-CD) film was prepared by a simple electropolymerization of a 20:1 mixture of the CD and the pyrrole monomer $LiClO_4$ supporting electrolyte. The resulting functionalized polymer film features interesting electrochemical properties such as selective, simultaneous and quantitative detection of some organic compounds of interest such as polyhydroxyphenyls and neurotransmitters derived from pyrogallol and catechol. The fabricated electrochemical sensor exhibits a fast and reversible linear response toward catechol within the concentration range of 1.5×10^{-7} to 8×10^{-6} M and towards pyrogallol within the concentration range of 1×10^{-6} to 1×10^{-5} M. The detection limit was 4×10^{-7} and 1.8×10^{-6} M for catechol and pyrogallol, respectively. Studies of neurotransmitters such as epinephrine, metanephrine and L-dopa (L-3,4-dihydroxyphenylalanine), showed better response toward epinephrine and L-dopa than for metanephrine. Calibration curves for these two neurotransmitters were linear over the concentration range of 1×10^{-6} to 1×10^{-5} M. The detection limit was 4×10^{-6} and 1×10^{-6}, respectively. The complexation capability of the Ppy/β-CD system is addressed here in terms of structure-electrochemical activity relationship. The mechanical stability of the film is also discussed. Measurements were performed using cyclic voltammetry (CV), scanning electron microscopy (SEM) coupled to energy dispersive analysis of X-ray (EDAX) and electrochemical impedance spectroscopy (EIS).

Keywords: β-Cyclodextrin; Polypyrrole; Polyhydroxyphenyls; Neurotransmitters; Electrochemical analysis

1. Introduction

Chemically modified electrodes offer unlimited possibilities for specific molecular recognition in the field of electrochemical monitoring of environmental or biological compounds of interest [1–3]. Among the wide range of electrode modifiers, perhaps one of the most attractive belongs to the cyclodextrin (CD) family [4]. The α-, β-, and γ-cyclodextrin rings contain six, seven and eight glucose units respectively and exhibit conical structures with a hydrophobic internal cavity and a hydrophilic exterior due to the presence of hydroxyl groups.

The well known ability of CDs to form supramolecular complexes with suitable organic and inorganic, neutral and ionic substances has resulted in the design of selective electrodes based on CDs [5,6]. The binding forces associated with the CD-guest inclusion formation are attributed to a number of factors, such as hydrophobic forces, hydrogen bonding, size of the cavity, shape of the guest molecule, and electrostatic interactions [7]. The behavior of pure self assembled monolayers (SAMs) of β-CD bound on gold electrodes was

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doi:10.1016/j.talanta.2004.10.003

investigated [8,9]. To facilitate sorption onto the gold electrode, all seven primary −OH groups of β-CD were converted into SH groups. The results showed that lack of favorable lateral interactions between the CD units induced density defects in the organization of CDs. Positively charged β-amino-CDs were also electrostatically immobilized as an ad layer on an SAM of thioctic acid on gold [10]. Unfortunately, the CD did not form a compact monolayer owing to repulsive coulombic interactions between the CD neighboring receptors.

The antagonism between the remarkable complexing properties of CDs and their lack of stability in a pure CD film preparation have pushed some researchers into exploring the properties of CD-doped polymeric films for chemical electrode modification [11–13]. In these studies, cyclodextrin (conventional) polymeric films were either deposited on the electrode surface by polycondensation of soluble α-, β- and γ-CD pre-polymers with glutaric dialdehyde, or prepared using poly(acrylic acid) film incorporating β-CD as receptor and a ultra thin chemically grafted polyamine overlayer. A simpler synthesis method is desirable.

An alternative method for solubilizing CDs into polymeric films has recently been reported. The electrosynthesis of CD/polymer systems uses conducting polymers as starting materials for electrosynthesis at the electrode surfaces. To the best of our knowledge, the only reports are from Lepretre et al. [14], Deronzier and Moutet [15] and Hassner and Alexander [16], in which polymer films of CD(s) were prepared electrochemically on glassy carbon and platinum electrodes starting with pyrrole-derivatized CD. More recently, Temsamani et al. [17,18] obtained remarkable results with an electropolymerized film of polypyrrole associated with sulfated β-cyclodextrin.

Because of their high electronic conductivity, conducting polymers are promising materials for future technologies and applications [19,20]. The polymers are very frequently compared with classical electrode materials, such as metals and glassy carbon, in electroanalytical applications. Polypyrrole [21] is indeed one of the most often studied and used conducting polymers because of the relative stability of its oxidation state in air and water, and also because of its simple electrochemical preparation. Conventional electropolymerization of pyrrole monomer produces polypyrrole films characterized voltammetrically by one typical oxidation wave around 1 V. The shape of the anodic peak may vary depending on the supporting electrolyte used, solvent and other experimental conditions [22].

In this paper, we present the results of a one-step electrochemical synthesis of a highly stable polymer film prepared using the combination of pyrrole monomer and β-cyclodextrin (β-CD). This combination features both fast electrochemical synthesis with the exclusive conducting polymer properties preserved, and also remarkable electrochemical sensing performances towards organic molecules of some biological importance. The supramolecular complexation of the CD units enhances the sensitivity and the selectivity toward certains molecules. The synthesis and quantitative analysis were investigated using cyclic voltammetry (CV). The electrochemical properties and the morphology of the polymer film were investigated using electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM).

2. Experimental

2.1. Apparatus and reagents

Pyrrole (>97%) was used with no further purification, β-cyclodextrin and benzimidazole were obtained from Fluka Chemical Company (Switzerland). Catechol, pyrrogallol and resorcinol, were purchased from Sigma (New Jersey, USA). Ascorbic acid L(+) was from Sigma (Barcelona, Spain). The supporting electrolyte salt, $LiClO_4$, was from Aldrich (Switzerland). L-Dopa, D-dopa, L-epinephrine L-dopamine, D,L-norepinephrine and metanephrine were purchased from Aldrich (Milwaukee, USA) and used as received. Deionized doubly distilled water (Autostill^{TM} Double D Still, from Jencons Scientific Ltd. and ELGA B114 deionizer), with a measured resistance of less than 15 $\mu S\,cm^{-1}$, was used for preparation of all solutions. The nitrogen (98%, grade R), used to purge the electrochemical reaction media, was obtained from Air Liquide (Tétouan, Morocco). All other chemicals used were of analytical reagent grade and used without further purification.

All electrochemical experiments were carried out in a three-electrode thermostated glass cell at 20 °C. All potentials were measured versus a saturated calomel reference electrode (SCE) with a Pt auxiliary electrode. A glassy carbon electrode (0.35 mm diameter) was used as the working electrode and its surface was polished with 0.5 μm alumina powder then cleaned by ultrasonication prior to the polymer electropolymerization.

Cyclic voltammetry (CV) experiments and EIS measurements were performed with a Voltalab® 10 type PGZ 100 from Radiometer (Villeurbanne, France). The impedance spectra were recorded using the same three electrode-cell setup described above in this paper. The initial frequency used was 100 kHz and the final one was 10 mHz with an AC amplitude of 5 mV. The potential of 0 V was chosen in order to insure the stability of the films on the electrodes during the experiment.

Scanning electron microscopy (SEM) and energy dispersive analysis of X-ray (EDAX) measurements of the polymer films were taken at the University of Cadiz (Spain) with a JSM 820 instrument (JEOL, Japan) operating at 30 keV and equipped with a Microanalyzer AN/10000.

2.2. Poly(Py-β-CD) film preparation

Polymer films were electrochemically prepared by electrodeposition from an aqueous solution of a 20:1 mixture of β-CD and pyrrole monomer (20 mM of pyrrole and 1 mM of the β-cyclodextrin) in 0.1 M of LiC1O$_4$ as supporting electrolyte. The polymerization was carried out using glassy carbon as the working electrode. Either a potentiostatic or a galvanostatic mode was employed for film growth. In most cases, after nitrogen purging (15 min), cyclic voltammetry was initiated and electrochemical synthesis started by scanning toward positive potentials from 0.0 to 1.8 V versus SCE at a scan rate of 50 mV s^{-1}. The scanning was stopped after 35 cycles corresponding to a steady state. A typical black film of poly(pyrrole-β-CD) could then be observed at the electrode surface. All experiments were performed under nitrogen atmosphere at 20 °C. These experimental conditions are maintained constant to ensure reproducibility of the film properties.

3. Results and discussion

3.1. Voltammetric behavior of poly(Py/β-CD) and Ppy films

The voltammograms of the electrosynthesis of Ppy and poly(Py-β-CD) from 0 to 1.8 V are presented in Fig. 1a and b. Clearly, quite different electrochemical behavior of the pyrrole electro-oxidation under the two situations can be observed. Fig. 1a shows the electro-oxidation of pyrrole in 0.1 M LiClO$_4$ aqueous solutions, with a first strong oxidation occurring around 1 V. In the following cycles, a steady-state is reached almost immediately. A black/brownish film grows on the electrode surface during the electropolymerization process. It is interesting that for the poly (Py-β-CD) (Fig. 1b), by CV scanning from 0 to 1.8 V, two oxidation peaks appear during the positive scan; the first peak occurs at 1 V and the second at 1.35 V. In contrast to the Ppy CV, the current increases slightly as a result of continuous cycling. This might be due to an increase in the active area on the electrode surface due to continuous deposition of Ppy(Py-β-CD) (according to Randles–Sevick equation [23]). A steady state occurs after 35 cycles. The slight positive shift of part of the oxidation peak compared to Ppy might be a result of the hydrophobic pyrrole partly or entirely included in the CD hydrophobic core. This inclusion does not seem to inhibit the pyrrole unit from polymerization. Indeed the remaining peak at 1 V indicated that part of the pyrrole units stay outside of the β-CD. CV measurements performed after several days of storage in deionized water show no change in the voltammetric response of the poly(Py-β-CD) films.

3.2. Morphology of Ppy and Ppy/β-CD films

SEM experiments were performed on both Ppy and poly(Py-β-CD) films, as shown in Fig. 2a and b. The pictures clearly show different organization modes. The Ppy prepared at glassy carbon shows the classical cauliflower relief, which is in agreement with reports of Ko et al. [24]. Surprisingly,

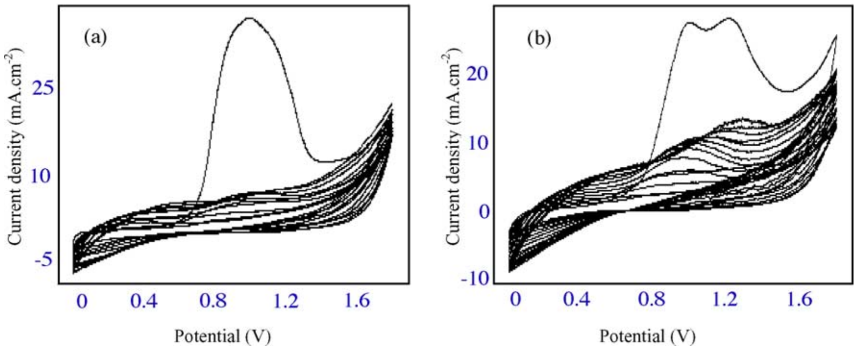

Fig. 1. Cyclic voltammograms for the electropolymerization of (a) 210^{-2} M pyrrole and (b) 1 mM pyrrole-β-CD in 0.1 M LiClO$_4$ aqueous solution; 35 sweep segments from 0 to 1.8 V. Solution was bubbled with N$_2$ for 15 min before electrosynthesis.

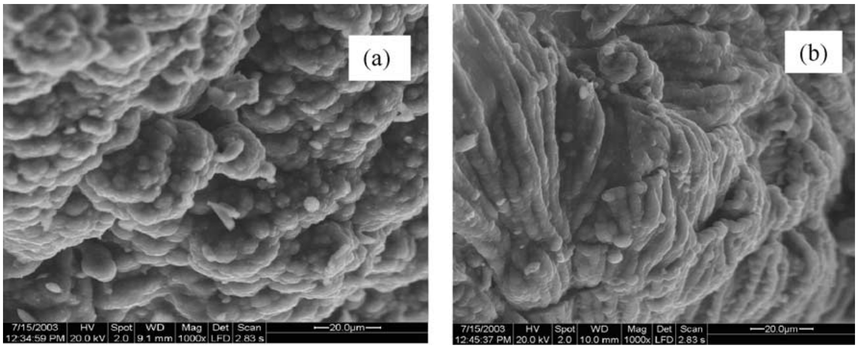

Fig. 2. Scanning electron micrographs of Ppy (a) and Ppy/β-CD) (b) films obtained at 30.0 kV with a 1000× magnitude.

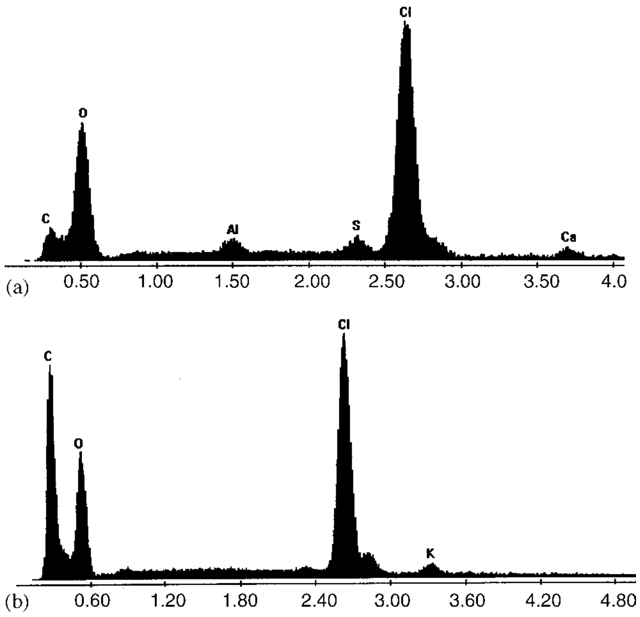

Fig. 3. EDAX spectra of Ppy (a) and Ppy/β-CD) (b) in LiClO$_4$. Conditions are as in Fig. 2.

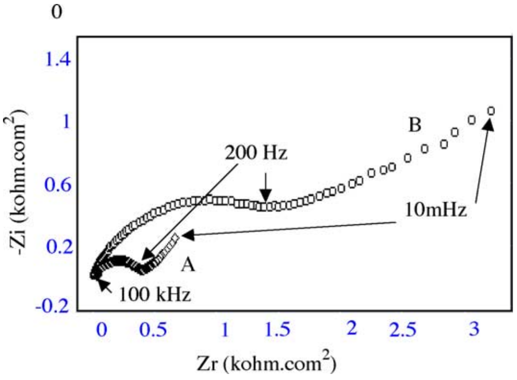

Fig. 4. Nyquist plot for impedance data obtained at 0 V from Ppy films (A) and (B) Ppy/β-CD prepared at glassy carbon; frequency range 100 kHz to 10 mHz.

the Ppy/β-CD system shows more oriented and organized structures. (Fig. 2b). The latter is in agreement with results of Amabilino et al. [25] and Nelson and Stoddart [26], where it has been shown that CDs may form pseudopolyrotaxanes with linear polymers. According to these authors, individual CD beads may slide along and rotate around the polymer axes, allowing glucose units of cyclodextrin to orient themselves to achieve the most favorable configuration and maximize their binding interactions. This could explain the linear mode growth observed in Fig. 2b.

To obtain more evidence on the presence of the β-CD inside the prepared polymer films, we have performed EDAX measurements on both pure Ppy and Ppy synthesized with β-CD films. Fig. 3a shows the EDAX spectrum of a film of pure Ppy and Fig. 3b shows the spectrum of the Ppy/β-CD system. It appears clearly from these results that the carbon content is substantially increased in the case of the films made of polypyrrole and CD (Fig. 3b) as compared to pure Ppy. According to our experimental conditions, the increase of the carbon quantity can only be the result of the incorporation of glucose units of the β-CD into the polymer film during electropolymerization. These results, present evidence that in spite of the well known solubility of the CDs, our synthesis method allow β-CD to incorporate and stabilize inside the polypyrrole conducting polymer films.

3.3. EIS measurements

Once the polymeric film was grown on the electrode surface, impedance experiments were performed to characterize the electrode/polymeric film/electrolyte interface. Fig. 4 shows typical impedance spectra of the Ppy (A) and Ppy/β-CD (B) electrodes in 0.1 M of LiClO$_4$ recorded at 0 V (versus SCE), frequency range of 100 kHz to 10 mHz and amplitude of 5 mV.

It appears clearly from this figure that the scales are very different for the two systems. The presence in the polymer films of β-CD seems to influence the interfacial impedance value. As can be seen in Fig. 4, the Nyquist plots are constituted of two regions: a depressed semicircle at high frequencies associated with charge transfer at the polymer/solution interface and a second region consisting of a straight line at 45° indicating a diffusionally-controlled process at the electrode. The diameter of the semicircle related to Ppy/β-CD is larger compared to pure Ppy electrodes. Based on the Randles equivalent circuit model [27] with a modification taking into account the presence of a porous interface [28] on the electrode, electrical parameters were calculated using Voltamaster® 4.0 software. The results are summarized Table 1. R_e is the electrolyte resistance while R_{ct} is the charge transfer resistance. C_d is the double layer capacitance at the electrode/solution interface. The observed decrease in the R_{ct} in the case of Ppy/β-CD means that charge transfer at this interface is higher than for the polypyrrole electrode. On the other hand, the higher value of the capacitance (C_d) of the electrical double layer at the Ppy/β-CD electrode may be a result of an increase in the electrode surface area [28]. This is in total agreement with the cyclic voltammetry results in Fig. 1.

Table 1
Electrical parameters calculated from the impedance spectra in 0.1 M of LiClO$_4$, for the Ppy and Ppy/β-CD/solution interfaces

	R_e ($\Omega\,cm^{-2}$)	R_{ct} ($k\Omega\,cm^{-2}$)	C ($mF\,cm^{-2}$)
Ppy	4.0	0.55	1.3
Ppy/β-CD	3.6	0.32	1.4

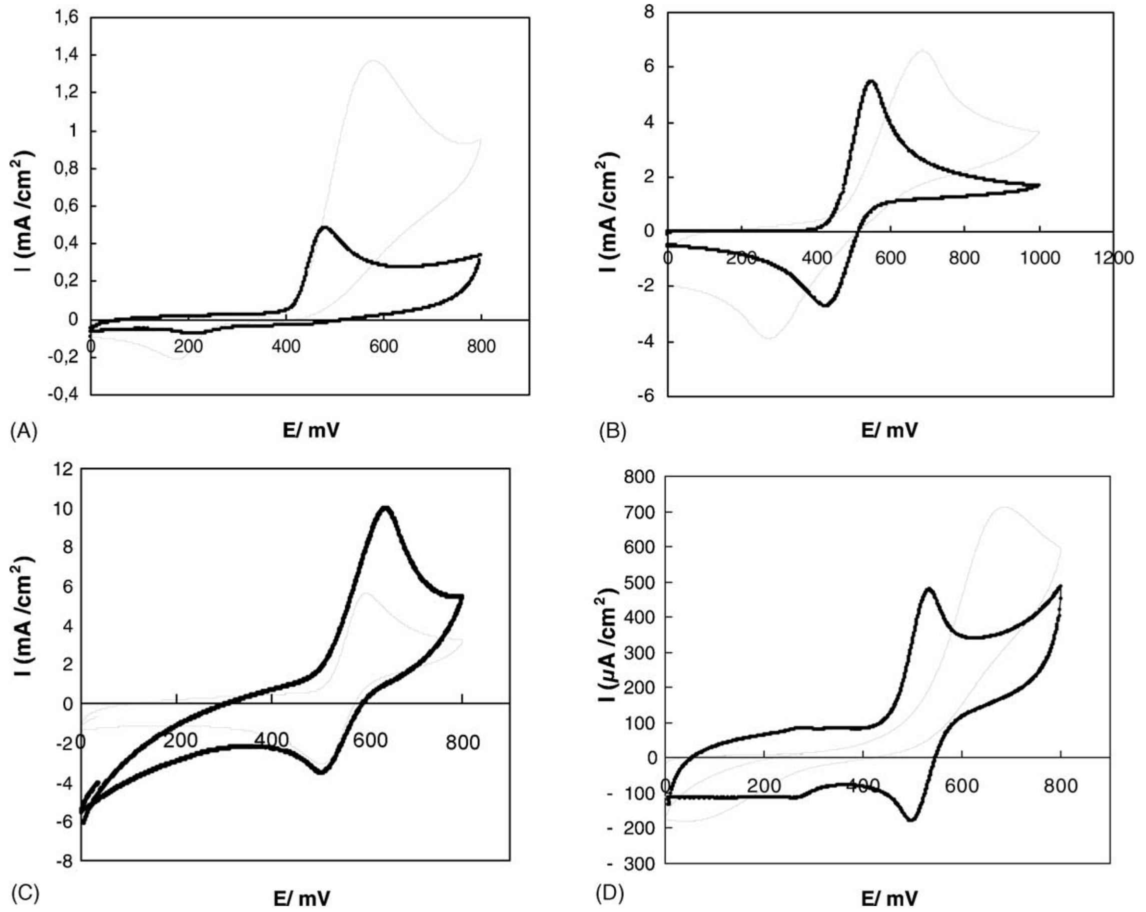

Fig. 5. Cyclic voltammograms at (. . .): glassy carbon, (—): Ppy/β-CD electrodes; 210^{-3} M (A) pyrogallol, (B) catechol, (C) epinephrine and (D) L-dopa. Scan rate, 50 mV s^{-1}; supporting electrolyte, 0.1 M H_2SO_4; $T = 20\,°C$.

3.4. *Electrochemistry of neurotransmitters and polyhydroxyphenols at bare glassy carbon and Ppy/β-CD electrodes*

Fig. 5 shows the CV behavior for pyrogallol (A), catechol (B), epinephrine (C) and L-dopa (D) at Ppy/β-CD and bare glassy carbon (GC) electrodes. From these voltammograms performed in 0.1 M H_2SO_4 (optimal supporting electrolyte condition), it appears that pyrogallol is the only molecule with non-reversible electrochemical behavior at GC with a small cathodic peak appearing at Ppy/β-CD at about ∼0.2 V. It also appears clearly that catechol, L-dopa, and epinephrine voltammograms are more reversible and exhibit sharper peaks at the Ppy/β-CD than at bare glassy carbon. The oxidation potentials of all these molecules are lower than those obtained in the case of bare glassy carbon, while the reduction potentials become more positive. In general, the results Fig. 5 show improved electrode kinetics at Ppy/β-CD electrode relative to bare GC.

The oxidation potentials into 0.1 M H_2SO_4 of various analytes (neurotransmitters, polyhydroxyphenyls and some tricyclic anti-depressive drugs) are compared for three different electrode systems: Ppy/β-CD, Ppy and glassy carbon (Table 2). These data were obtained using a positive scan at a rate of 50 mV s^{-1}. All analytes were in contact with the electrolyte solution for 10 min prior to the CV measurements. In all case, except for imipramine, the E_{pa} (the anodic potential) values were decreased on the Ppy/β-CD relative to the measured E_{pa} at bare GC. It is interesting to note that under the same experimental conditions (0.1 M H_2SO_4), L-dopa, D-dopa, benzimidazole and imipramine do not show any peak at the Ppy electrode, while their response becomes fast and reversible with better defined peaks at the Ppy/β-CD electrode. The two neurotransmitters epinephrine and L-dopa also show improved electrochemical behavior at Ppy/β-CD electrode while metanephrine do not undergo any improvement keeping a response closer to the one on GC. If we assume the hypothesis of “drug incorporation”, we can say that the steric bulk of the methoxy group may exclude part of the metanephrine from incorporating into the hydrophobic β-CD cavity. In any case, substitution on the meta position has been reported to reduce retention on cyclodextrin chromatographic phases [29]. However, these metanephrine suggested mechanisms need further experimentation.

The large residual current observed under analyte-free supporting electrolyte appears to be an inherent property of

Table 2
Oxidation peak potentials of some investigated compounds 1 mM at three different electrodes.

Compounds	E_p[a] (V)		
	Glassy carbon	Ppy	Ppy/β-CD
Metanephrine	0.948	0.707	0.509
Norepinephrine	0.900	0.544	0.542
Epinephrine	0.806	0.538	0.520
Dopamine	0.786	0.513	0.530
D-Dopa	0.609	–[b]	0.541
L-Dopa	0.789	–[b]	0.533
Catechol	0.728	0.531	0.432
Resorcinol	1.059	0.721	0.631
Pyrogallol	0.498	0.510	0.482
Benzimidazole	0.618	–[b]	0.569
Hydroquinone	0.792	0.565	0.502
Chlorpromazine	0.801	0.780	0.701
Imipramine	1.08	–[b]	0.953

[a] Values are obtained from a positive scan in 0.1 M H_2SO_4. Scan rate 50 mV s^{-1}.
[b] No peak was observed.

conducting polymers [30]. It seems that the large surface area provided by the three-dimensional porous structure of the film greatly increase both faradaic and non-faradaic residual currents. This phenomenon has been observed by other workers with polypyrrole [30] and poly-3-methylthiophene (P3MT) [31]. The transport mode towards the Ppy/β-CD electrode was determined from ip_a versus the square root of the scan rate supports a diffusion-controlled process at the electrode interface. The correlation coefficient $R^2 > 0.99$ of all tested molecules.

A calibration curve for pyrogallol, catechol, L-dopa and epinephrine detected at Ppy/β-CD electrodes was drawn. The graph shows linear response for all the substances studied inside the indicated concentration range. The estimated detection limits for $S/N > 3$ were 4×10^{-7} M for catechol and 1.8×10^{-6} M for pyrogallol. While for L-dopa and epinephrine the estimated detection limits were 1×10^{-6} and 4×10^{-6} M, respectively.

4. Conclusion

The concept of chemically modified electrodes was developed to fulfill the need for controlling the reactivity, sensitivity and selectivity of the electrode reactions in many applications. Ppy/β-CD films formed under our electropolymerization conditions are very compact, stable and offers interesting electrocatalytic properties. In this work, we believe that the β-CD plays a key role in the improved sensing properties of the new film which is totally different from the work of Chane-Ching et al. [32] where the β-CD played a unique role of a inclusion compound that catalyses the electropolymerization of low water soluble dipyrrolyl monomers. In that later case, β-CD remains in the aqueous phase with no traces in the resulting conducting polymer films.

From an analytical point of view, the fabricated Ppy/β-CD films, exhibits improved electrochemical reversibility toward some polyhydroxyphenyls. A structure-activity relationship study is underway in order to understand the possible role of the methoxy group of metanephrine on its poor electrochemical signal an therefore "possible partial exclusion" from the β-CD cavity. Epinephrine and L-dopa do not have any metoxy function into their chemical structure and therefore could be detected more easily also on GC electrode. Another fact to bear in mind is that some β-CD may form rotaxanes with the polypyrrole and some others not. This means that not all the CDs have room in their interior cavity to fit the organic molecules present in the system. A new form of electrochemical selectivity may be induced. This phenomenon is good enough to show different electrochemical behaviors. In any case, the performances obtained for certain molecules, make this polymer films a material which has potential for future analytical applications.

Acknowledgements

This project was possible thanks to the Moroccan Ministry of Higher Education through the program PROTARSII: P21/96 and PARS: CHIM 044. We would like to express our gratitude to the K.L. Cheng Trust for his symbolic financial contribution.We would like to thank Professor José Luis Hidalgo de Cisneros from the University of Cadiz for his kind help in performing SEM measurements.

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