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Immobilization of lutetium bisphthalocyanine in nanostructured biomimetic sensors using the LbL technique for phenol detection

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ABSTRACT

This study describes the development of amperometric sensors based on poly(allylamine hydrochloride) (PAH) and lutetium bisphthalocyanine ($LuPc_2$) films assembled using the Layer-by-Layer (LbL) technique. The films have been used as modified electrodes for catechol quantification. Electrochemical measurements have been employed to investigate the catalytic properties of the $LuPc_2$ immobilized in the LbL films. By chronoamperometry, the sensors present excellent sensitivity (20 nA μM^{-1}) in a wide linear range ($R^2 = 0.994$) up to 900 μM and limit of detection ($s/n = 3$) of 37.5×10^{-8} M for catechol. The sensors have good reproducibility and can be used at least for ten times. The work potential is +0.3 V vs. saturated calomel electrode (SCE). In voltammetry measurements, the calibration curve shows a good linearity ($R^2 = 0.992$) in the range of catechol up to 500 μM with a sensitivity of 90 nA μM^{-1} and LD of 8 μM.

1. Introduction

The ability to detect phenolic compounds is of great interest in medical, environmental and food industry (Queimada et al., 2009; Mahugo Santana et al., 2009). The study of phenolic compounds in wine industry is of particular interest for quality of wine to guarantee its authenticity and organoleptic characteristics, thus representing an economical and health appeal (Parra et al., 2006; Bergonzi et al., 2008; Saura-Calixto and Díaz-Rubio, 2007). For example, it has been found that the type of red wine ageing is characterized by phenolic composition (Monagas et al., 2006; Apetrei et al., 2007). In addition, regular consumption of red wine can reduce coronary heart diseases (this hypothesis is well known as French Paradox) (Del Rio et al., 2010; Rivero-Pérez et al., 2008).

Among the available methods used to quantify polyphenols in red wines, electrochemical sensors are the best choice due to the low cost and simplicity. The development of electrochemical sensors driven by self-assembled thin films technology, in particular, are of special interest, due to the great potential of miniaturization exhibited by these systems (Cabaj et al., 2009; Schmidt et al., 2008). Therefore, layer-by-layer assembly has been successfully employed to fabricate thin films for sensing devices (Mattoso et al., 1995; Zucolotto et al., 2006; Siqueira et al., 2008).

The most used biosensors for the detection of phenols are those based on tyrosinase enzyme. Tyrosinase (also called polyphenol oxidase) is a dicopper metalloprotein (Lind et al., 1999) that carries out the aerobic oxidation of a phenolic compound to its correspondent catechol (cresolase reaction) and then converts the o-diphenol to o-quinone (catalase reaction) (Lind et al., 1999). However, the low enzyme stability, specific activity and significant inhibition of the immobilized tyrosinase by caused by the reaction products can influence in the response of this type of sensors. To overcome such limitations, efforts have been made on the use of synthetic enzymes as tyrosinase substituent. Metallophthalocyanines can be used as artificial enzyme due to the similar structure of the prosthetic group of heme proteins and the central coordinated metal atom. For example, Kobayashi et al. (Kobayashi et al., 1992) used cobalt phthalocyanine adsorbed at pyrolytic graphite electrode to mimic the prosthetic group of peroxidase. Sotomayor et al. have studied the use of copper phthalocyanine as enzymeless biosensor to the determination of phenolic compounds (Del Pilar Taboada Sotomayor et al., 2002).

The interest of metallophthalocyanines applied in sensor devices comes from their physical and chemical stability, commercial availability and electrochemical properties with rich redox chemistry (Guillaud et al., 1998). Phthalocyanines have shown interesting electrocatalytic effects that facilitate the oxidation of phenols (Casilli et al., 2005). The possibility of mimic natural enzymes makes the phthalocyanines best candidates to artificial enzymes (Lever, 1999). In previous papers, phthalocyanines were

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immobilized either using carbon paste electrodes (Apetrei et al., 2007) or the Langmuir-Blodgett (LB) technique (Pavinatto et al., 2011). Besides being fast and cheap, the former method has the disadvantage of the slow kinetics and poor reversibility of the processes observed. In contrast, the LB technique, gives rise to well resolved peaks and fast kinetics. On the other hand, LB is a time-consuming and expensive technique.

The use of metallophthalocyanines allows efficient electron mediator effect for phenols biosensing using the LB technique (Pavinatto et al., 2011). We have demonstrated, for example, the enhancement in the sensitivity of biosensor based on lutetium bisphthalocyanine ($LuPc_2$) (Apetrei et al., 2011a). Our method is related to the work of Cabaj et al. (Cabaj et al., 2009), where the tyrosinase enzyme is immobilized on an amphiphilic layer of arachidic acid, using the $LuPc_2$ as electron mediator. In that study, we observed that the $LuPc_2$ exhibit catalytical property and can be used in enzymeless biosensor. That suspicion would be confirmed and published in a recent paper (Pavinatto et al., 2011).

In this study we propose a different approach to prepare sensors based on bisphthalocyanines consisting in the use of the LbL technique. This technique is usually used to immobilize alternate monolayers of soluble phthalocyanines and polycations. However, in a recent work, our group has developed a method to prepare LbL films of insoluble iron phthalocyanines, taking advantage of the interactions between the NH groups of the polycation and the metallic ion of the metallophthalocyanine (Alessio et al., 2010). For this purpose, we fabricated amperometric sensors based on lutetium bisphthalocyanine ($LuPc_2$) and poly(allylamine hydrochloride) (PAH) films assembled using the LbL technique. The films were used as modified electrodes for catechol quantification. Among the phenolic compounds, catechol is one of the most important due to its enzyme catalysis and as a molecular model for other ones. Catechol was used as substrate representative of phenolic compounds being a better substrate of tyrosinase enzyme as reported in literature (Mita et al., 2007). The catalytic activity for catechol was assessed using data obtained by voltammetry and chronoamperometry.

2. Experimental

$LuPc_2$ was synthesized through the direct reaction of 1,2-dicyanobenzene (phthalonitrile) with lutetium acetate according to a previous publication (Linaje et al., 2000). ITO-covered glass electrodes were purchased from Delta Technologies. Phosphate buffer solutions (PBS, 0.1 M, pH 7.0) were prepared from K_2HPO_4 and KH_2PO_4 (Sorensen's phosphate buffer).

All chemicals used were of analytical grade and used without any further purification. The ultrapure water used for LbL films and electrochemical experiments were obtained from a Milli-Q water system (resistivity of 18.2 MΩ cm).The LbL films were made through the alternating deposition of $LuPc_2$ and poly(allylamine hydrochloride) (PAH): firstly, the electrodes were immersed in a PAH solution (water, 1 g/L) for 3 min, then rinsed in a water solution for few seconds and gently dried in a N_2 flux. The second layer was formed by the immersion of the electrode in a $LuPc_2$ solution (chloroform, 1 g/L) for 3 min, and dried on air. The process could be repeated until the desired number of PAH/$LuPc_2$ bilayers had been adsorbed. All experiments were carried out at room temperature (25 °C). Roughness measurements of the films were performed with a Veeco Dektak 150 surface profilometer. Electrochemical measurements were carried out in a potentiostat/galvanostat (Autolab, Princeton) using a conventional three-electrode cell. The ITO conducting substrates covered with LbL films were used as working electrodes (work area of 0.6 cm × 1.0 cm). As reference and counter electrode, we used a saturated calomel electrode (SCE) and a Platinum plate (0.5 cm × 1 cm), respectively. Cyclic voltammograms were registered in a cell volume of 10 mL. Chronoamperometric measurements were performed under an applied potential of +0.3 V (vs. SCE) by successive addition of catechol 50 μM (cell volume of 10 mL). All experiments were carried out at room temperature (25.0 °C). The catechol solution was prepared in phosphate buffer (0.01 M, pH 7.0). The response current was recorded after 2 min. Before each measurement, the solution was gently stirred for 1 min (for the homogeneity of the solution) and the system was put in open circuit in the same period of time. All standard solution of catechol was freshly prepared before each experiment.

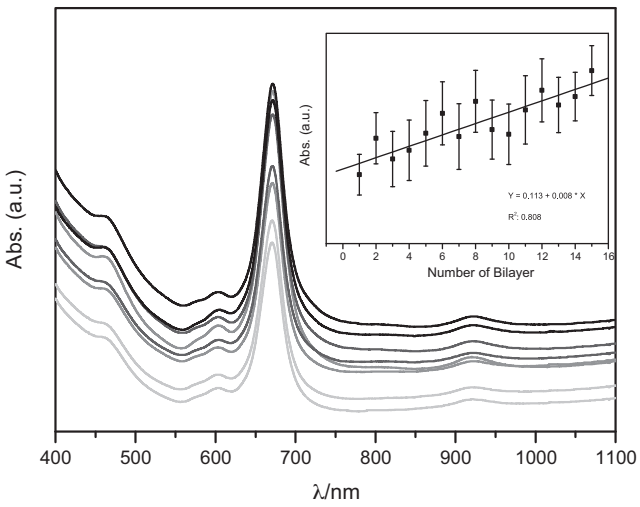

Fig. 1. UV–vis absorption spectra of the PAH/$LuPc_2$ containing different numbers of bilayers. Inset shows the growth of the film by the linear dependence of the absorbance at 662 nm as a function of bilayer number (each point is the average value for 3 different substrates) (R^2 = 0.808).

3. Results and discussion

3.1. The PAH/$LuPc_2$ LbL film

Chloroform solution of the $LuPc_2$ shows an intense Q-band at 662 nm $LuPc_2$ accompanied by a shoulder at 596 nm. The B-band (or Sored band) appear at 320 nm (Rodríguez-Méndez et al., 1993). The UV–vis absorption spectra of the $LuPc_2$ in chloroform solution and for a 15 bilayers PAH/$LuPc_2$ film are shown in SD 1. The B and Q bands are assigned to $\pi \rightarrow \pi^*$ transitions of the phthalocyanine ring (Ishikawa and Kaizu, 1996). Weak bands at 456 and 574 nm associated with the unpaired electron of the phthalocyanine can also be observed. Because of the radical character of the $LuPc_2$ a band at 920 nm also appears in the spectra (Saydam et al., 2009). A comparison between the spectra of $LuPc_2$ in solution and LbL film revealed that the Q-band was a little broader and red shifted on the PAH/$LuPc_2$ film. The band at 320 nm and 920 nm did not vary for both $LuPc_2$ in solution or in the LbL film. The bathochromic shift of 12 nm of the Q-band in the LbL film is probably caused by J-aggregates in head-to-tail arrangement of transition dipoles in the film (Del Caño et al., 2002). The broadening can be associated to the extension of the aromaticity due to the ordering induced by the LbL technique.

Film growth was monitored by measuring the maximum absorption of the Q-band of the phthalocyanine upon deposition of successive bilayers. According to the Lambert-Beer law, the linear growth (R^2 = 0.808) indicates the deposition of the same mass of material for each bilayer. This is illustrated in Fig. 1 where the absorbance of the Q-band is plotted vs. the number of bilayers. The absence of a shift of the absorbance maximum as a function of

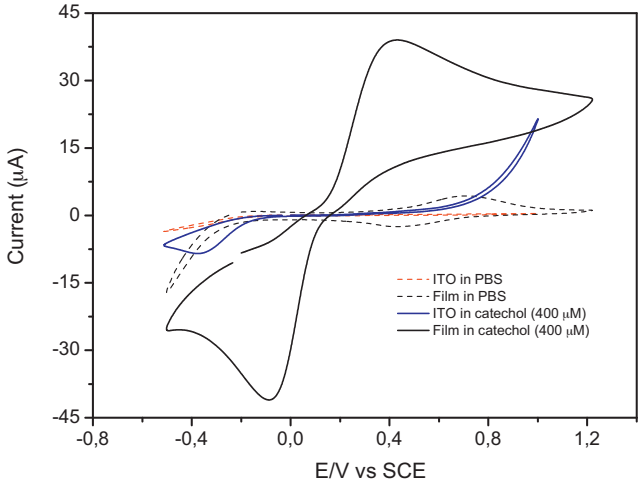

Fig. 2. Cyclic voltammograms using ITO and PAH/$LuPc_2$ LbL film (2 bilayers) as working electrodes in phosphate buffer (PBS, 0.1 M, pH 7.0) in absence (dashed line) and presence (continuous line) of catechol (400 μM) in PBS (0.1 M, pH 7.0) at scan rate of 0.1 V s^{-1}.

the number of bilayers, as described in Fernandes et al. (Fernandes et al., 2010), allow us to infer the homogeneity of the film. The optical microscopy and roughness measurements (see supplementary data) confirm this assumption.

3.2. Electrochemical characterization of the PAH/$LuPc_2$ LbL film

In order to evaluate the electrochemical response of the films, cyclic voltammograms (CVs) were registered in phosphate buffer (0.1 M, pH 7.0). The sensing properties of ITO and $[PAH/LuPc_2]_2$ LbL films were tested towards catechol solution (400 μM in phosphate buffer at 0.1 M, pH 7.0) at 0.1 V s^{-1} (Fig. 2). As expected, voltammograms registered in PBS using bare ITO did not show any noticeable response. ITO immersed in catechol exhibits two peaks at ca. 0.6 V (anodic) and at ca. −0.2 (cathodic) vs Ag/AgCl (Casilli et al., 2005). The absence of the anodic peak for the ITO in catechol solution (400 μM) presented in Fig. 2 is probably because of the very small amount of catechol employed. The redox processes observed in $LuPc_2$ in PBS are due to the Pc ring (Apetrei et al., 2011a). The CV corresponding to LbL film (working electrode) immersed in catechol (black solid line) shows the peak at ca. 0.4 V due to catechol oxidation (Mu, 2006; Chen et al., 2009) (the same peak not is observed for bare ITO electrodes. In this case, only a small reduction peak appears). The reduction of the neutral form of the $LuPc_2$ can be observed at −0.2 V, when the LbL films are immersed in PBS, in accordance with our previous paper (Apetrei et al., 2011a). The oxidation of catechol exhibits two reversible peaks, as reported by Portaccio et al. (Portaccio et al., 2010); and the ratio I_{pa}/I_{pc} is almost equal to 1. The voltammetry shows that the oxidation of catechol is a quasi-reversible behavior in 1-electron transfer step. These results confirm that $LuPc_2$ has electrocatalytic activity towards the catechol oxidation, as expected. By the voltammograms, it is evident that the PAH/$LuPc_2$ LbL sensor shows low background currents.

The LbL electrodes were found to be stable even after 40 CV scans since no significant shifts in peaks potential were observed (SD 2). The first scan is slightly different from the second cycle, as expected. In the subsequent cycles, the voltammograms are highly reproducible with a decrease in the intensity of the peaks. The intensity decreased by 50% after 50 scans. Martín et al. reported an intensity decrease of 50% after 75 scans for electrophoretic deposition of $LuPc_2$ on ITO (Martín et al., 2010).

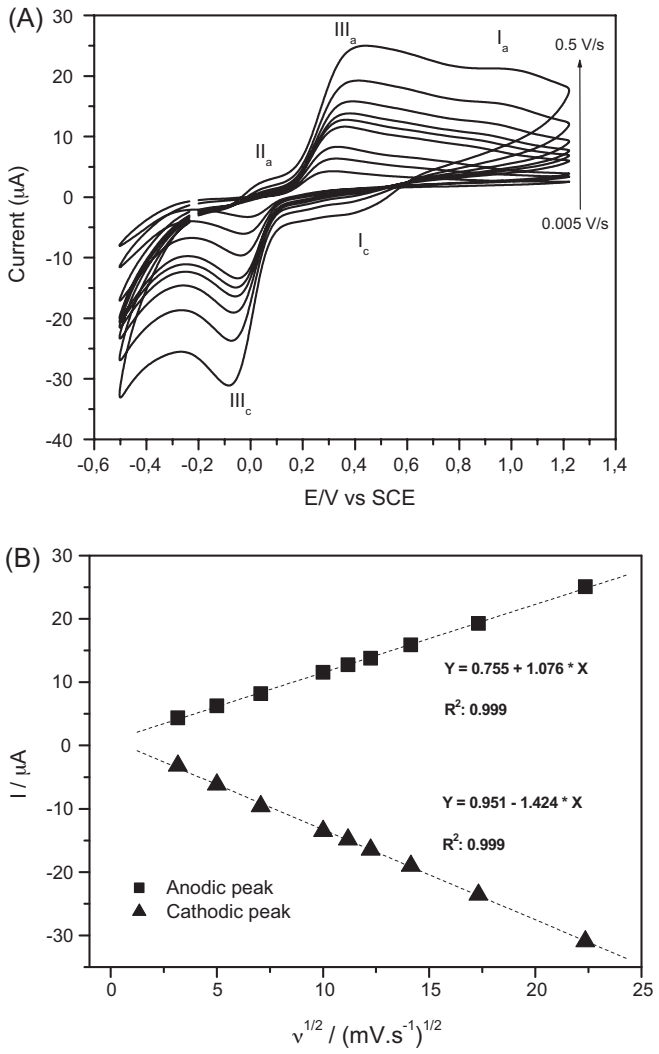

Fig. 3. Cyclic voltammograms at different scan rates (from 0.005 to 0.5 V s^{-1}) for a 2-bilayer LbL film of PAH/$LuPc_2$ (A). Linear relationship between peak intensity of the redox pair of the catechol (peak III) and square root of the scan rate (B). Supporting electrolyte: catechol 400 μM in PBS.

Fig. 3 shows the effect of scan rate (ν) on the cyclic voltammetric response of PAH/$LuPc_2$ LbL film in catechol solution. By increasing the scan rate, intensities of both anodic and cathodic peaks increased. This effect can be associated with the one electron ring oxidation of the neutral form of the $LuPc_2$ ($Lu(III)Pc_2/Lu(III)Pc^+$, peak I) and the one electron ring reduction of the $LuPc_2$ ($Lu(III)Pc_2/Lu(III)Pc^-$, peak II) (Arrieta et al., 2003; Liu et al., 1989). The voltammograms are quite similar to those described for $LuPc_2$ electrode obtained by electrophoretic deposition (Martín et al., 2010). The peak at ca. 0.9 V, associated to the oxidation of the $LuPc_2$, however, is not observed at Fig. 2. This is because the concentration of catechol is high, compared with the $LuPc_2$, and does not allow the observation of the small peak from phthalocyanine (at the adopted scan rate). Since the relative intensity of peaks related to catechol and $LuPc_2$ is constant, and the peak of $LuPc_2$ is less intense, it can be only observed at high scan rates (as shown in Fig. 3A). It is noticeable the shift of the anodic peak to more positive values and the shift of the cathodic peak to more negative ones upon increasing the scan rate. The same phenomenon was reported by Mersal et al. (2009) using screen printed graphite electrode for catechol electrochemical detection. The presence of catechol, an antioxidant agent, shifts the oxidation of the $LuPc_2$ to higher poten-

Table 1
List of references regarding catechol detection via amperometric electrochemical methods. Abbreviations: PAH: poly(allylamine hydrochloride); $LuPc_2$: lutetium bisphthalocyanine; CPE: carbon paste electrode; SWCP: single wall carbon nanotubes; Tyr: tyrosinase; GCE: glassy carbon electrode; GCPE: glassy carbon paste electrode; MIP: molecularly imprinted polymer based electrode; EP-co-Am: electrosynthesized poly(aniline-co-p-aminophenol); SCE: saturated calomel electrode.

	Sensor configuration	E_{appl} (mV)	Linear up to (μM)	Sensitivity (nA μM^{-1})	LD (μM)	Reference
Biosensors	PAH/$LuPc_2$	+300 vs. SCE	900	20	0.375	Here
	CPE-SWCP-Tyr	−150 vs. Ag/AgCl	120	138	0.02	(Mita et al., 2007)
	Pt-Laccase	−50 vs. Ag/AgCl	58	210	0.07	(Quan and Shin, 2004)
	GCE-Fe_3O_4-Tyr	−200 vs. SCE	70	514	0.025	(Wang et al., 2008)
	Bacterial cells based	−700 vs. Ag/AgCl	5	5.07	–	(Timur et al., 2003)
Sensors	Hybrid-MIP	+300 vs. Ag/AgCl	144	–	0.228	(Lakshmi et al., 2009)
	EP-co-Am	+550 vs. SCE	500	–	0.8	(Chen et al., 2009)
	GCPE	−100 vs. SCE	35	24	0.41	(Rodríguez and Rivas, 2002)

tials as reported by Martin et al. (Martín et al., 2010), which is more evident for high scan rates. From the plot, the peak intensity of the redox pair of the catechol (peak III at Fig. 3A) vs. the square root of the scan rate is shown in Fig. 3B. It can be seen that the peak current is proportional to the square root of scan rate in the range from 5 to 500 mV s^{-1}. This result indicated that the response current was controlled by diffusional process in charge transfer. The diffusion coefficient (D) can be estimated from the I_p vs. $v^{1/2}$ plot according to the Randles-Sevcik equation (Apetrei et al., 2011a):

$$I_p = 2.687 \times 10^5 n^{3/2} v^{1/2} D^{1/2} AC$$

where I_p is the peak current, A is the electrode surface area, and C is the bulk concentration. The estimated value for the diffusion coefficient, D, was 9.78×10^{-7} cm^2 s^{-1}. The calculated D is consistent with the values found for films based on electrophoretic deposition of $LuPc_2$ (Martín et al., 2010) and carbon paste electrode based on carbon nanotubes (Apetrei et al., 2011b).

To confirm the best-applied potential for the LbL film, the response current was recorded as a function of the applied potential in presence of catechol (400 μM). The anodic response current increased up to +0.4 V, after which the response current remained practically constant at value of ca. 10 μA (SD 3). About 80% of the response current is achieved at the chosen potential of +0.3 V.

3.3. Detection of catechol

Fig. 4 shows the electrochemical response of the PAH/$LuPc_2$ LbL electrode upon successive additions of catechol. The intensity of the peak at 0.4 V was linearly dependent on catechol concentration, as shown in the inset of Fig. 4. The response is highly reproducible with a standard deviation (n = 4) of ca. 2.2%, similar to what has been reported (Pavinatto et al., 2011). The calibration curve shows a good linearity (R^2 = 0.994) in the range of catechol up to 500 μM with a sensitivity of 90 nA μM^{-1}.

The chronoamperometric results for successive addition of catechol, at the potential level of +0.3 V vs. SCE in PBS (0.1 M, pH 7.0) is presented in Fig. 5. A calibration curve appears in the inset of Fig. 5. The calibration plot is the average of three distinct electrodes (values at time of 60 s). It is interesting to notice that the response current value of PAH/$LuPc_2$ LbL films for towards 500 μM of catechol is the same for a glassy carbon electrode (ca. 10 μA, catechol, applied potential of 0.305 V) (Rodríguez and Rivas, 2002). The relationship between the response current and catechol concentration presented a linear range from 0 to 900 μM (Fig. 5) (R^2 = 0.994). The limit of detection (LD) for catechol was calculated according to the 3S/b criterium (Mocak et al., 1997), where S is standard deviation (n = 10) of the blank (pure buffer) and b is the slope of the analytical curve. The LD was estimated at 3.75×10^{-7} M and 8×10^{-6} M to the chronoamperometric and voltammetric response, respectively. The sensitivity of PAH/$LuPc_2$ LbL film for catechol (angular coefficient of the I_p vs. [catechol]) is 20 nA μM^{-1}.

The reusability of the sensor was also investigated with respect to a certain concentration of catechol. The response signal was collected by successive amperometric measurements. The sensors could be used for at least 10 measurements with a decrease in the

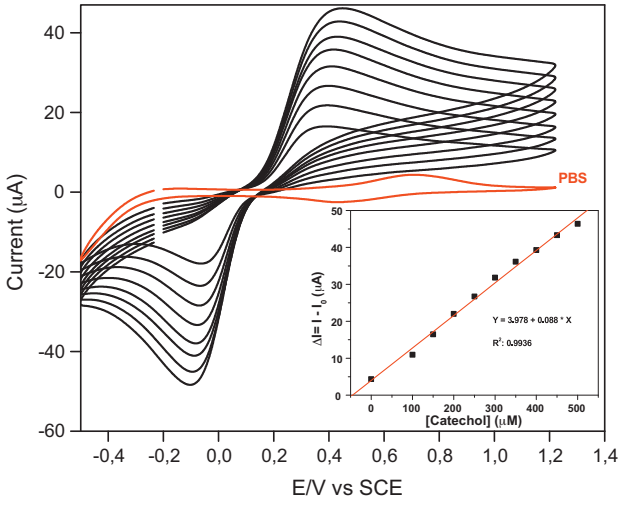

Fig. 4. Cyclic voltammograms recorded at 0.1 V s^{-1} in 0.1 M PBS (pH 7.0) for a 2-bilayer PAH/$LuPc_2$ film in the presence of catechol at concentrations from 50 to 500 μM. Inset: Calibration curve of [PAH/$LuPc_2$]$_2$ film obtained by cyclic voltammetry: intensity of the oxidation peak vs. catechol concentration at ca. +0.4 V.

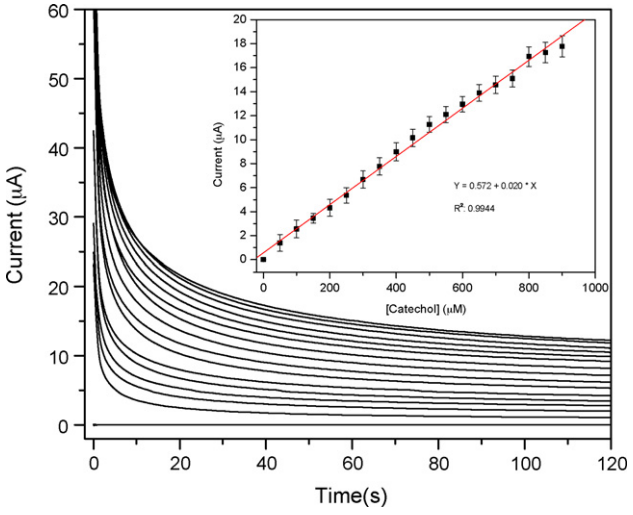

Fig. 5. Typical steady state current response by chronoamperometry of the sensor [PAH/$LuPc_2$]$_2$ toward an increasing concentration of catechol. Inset: calibration plot of the LbL sensor [PAH/$LuPc_2$]$_2$ toward catechol (each point is the average value for 3 different electrodes) (R^2 = 0.994). Supporting electrolyte: Phosphate buffer at 0.1 M. Applied potential: +0.3 V. Response time: 60 s.

response signal of ca. 7% (after the first measurement) (as shown in SD 4). Similar results were described by Serra et al. using a biosensor based on graphite–ethylene/propylene/diene–tyrosinase electrode (Serra et al., 2002). The reproducibility of sensor was examined for four sensors units resulting in a relative standard deviation (R.S.D.) of 3.0%.

The sensitivity of 20 nA μM^{-1} (working electrode area of 0.6 cm^2) was greater than the value of 9.6 nA cm^{-2} μM^{-1} reported for a biosensor based on tyrosinase modified carbon paste electrode (Hedenmo et al., 1997). It is worthwhile to mention that the linear range found for our biomimetic sensor system was better than all cited works with a LD comparable with some amperometric sensors, as demonstrated in Table 1.

4. Conclusions

This study presented the development of a polyphenol sensor based on LbL films of lutetium bisphthalocyanine ($LuPc_2$) and poly(allylamine hydrochloride) (PAH). We confirmed the catalytic activity of $LuPc_2$ for poliphenolic compounds. In voltammetry measurements, the PAH/$LuPc_2$ LbL sensor presented good linearity ($R^2 = 0.992$) in the range up to 500 μM with a sensitivity of 90 nA μM^{-1} and detection limit ($s/n = 3$) of 8 μM. By chronoamperometry, the sensors exhibited a wide linear range ($R^2 = 0.994$) up to 900 μM and limit of detection of 37.5×10^{-8} M (sensibility of 20 nA μM^{-1}) for catechol. The sensor has good reproducibility and can be reused at least for ten times with a decrease in the response signal of ca. 7% (after the first measurement). The PAH/$LuPc_2$ sensor covers a wide range of catechol concentrations, and seems to be suitable for the determination of polyphenols in real samples. Also important to emphasize is that the PAH/$LuPc_2$ LbL sensors developed here do not require the addition of hydrogen peroxide, common for other biomimetic sensors.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.bios.2011.05.032.

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