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SiO_2/C/Cu(II)phthalocyanine as a biomimetic catalyst for dopamine monooxygenase in the development of an amperometric sensor

Abdur Rahim, Sergio B.A. Barros, Lauro T. Kubota, Yoshitaka Gushikem*

Institute of Chemistry, State University of Campinas, PO Box 6154, 13083-970 Campinas, SP, Brazil

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ABSTRACT

A mesoporous carbon ceramic SiO_2/50 wt% C (S_{BET} = 170 $m^2\ g^{-1}$), where C is graphite, was prepared by the sol–gel method. This material was used as matrix to support copper phthalocyanine (CuPc), prepared in situ on their surface, to assure homogeneous dispersion of the electrocatalyst complex in the pores of the matrix. Pressed disk electrodes made with SiO_2/C/CuPc was tested as amperometric sensors for dopamine. Under optimized conditions, at −20 mV vs SCE in 0.08 mol dm^{-3} Britton–Robinson buffer (BRB) solution (pH = 6.0) containing 100 μmol dm^{-3} of H_2O_2, a linear response range for dopamine from 10 up to 140 μmol dm^{-3} was obtained with a sensitivity of 0.63 (±0.006) nA dm^3 μmol^{-1} cm^{-2} and the limit of detection LOD was 0.6 μmol dm^{-3}. The sensors presented stable response during successive determinations. The repeatability, evaluated in terms of relative standard deviation of 1.37% for n = 10 and 10 μmol dm^{-3} dopamine. The response time was 1 s and lifetime 9 months. Finally, the sensor was tested to determine dopamine in the sample, and gives very good results for its determination. The presence of other phenols like catechol and resorcinol did not show any interference in the detection of dopamine on this electrode, even in the same concentration with the dopamine.

1. Introduction

The attractive features of most carbon ceramic electrodes (CCEs) include chemical inertness, physical rigidity, and tunable porosity that lead to significant advantages in the design and development of electrochemical sensors [1–3]. Furthermore, they can be modified either by adsorption (surface modification) or entrapment during formation (bulk modification).

In the CCE based on SiO_2/C-graphite shows good electrical conductivity provided by the interconnected graphite particles inside the matrices. These materials have been employed to develop electrochemical sensors [3] and the recent literature has reported the determination of NADH [4,5], BrO^{3-} and IO^{3-} [6] the simultaneous determination of dopamine, ascorbic and uric acid [7] and oxalic acid sensor [8].

Dopamine (DA) is one of the most important catecholamines and belongs to the family of excitatory chemical neurotransmitter. It plays a very important role in the function of central nervous, cardiovascular, renal and hormonal systems, as well as a key role in the drug addiction. Abnormal levels of DA lead to brain disorders such as Parkinson and schizophrenia diseases [9,10]. In addition, DA is involved in the regulation of cognitive functions such as attention, stress, rewarding behavior, and reinforcing effects of certain stimuli [11].

The catecholamines, like dopamine, are present in large amounts in different drugs and many efforts to develop simple, rapid, and accurate analytical procedure for their determination are being done. In the literature different methods have been described for dopamine determination in biological samples and pharmaceutical formulations, such as spectrometry [12,13] chromatography [14,15] chemiluminescence [16] and electrochemistry [17–19].

In the electrochemical methods, amperometric biosensors have shown great potential for developing versatile analytical techniques for catecholamine's determination [20–27]. In recent years, interest in obtaining a more efficient electron transfer between the active site of the enzyme and the electrode surface, in order to infer more sensitivity to the biosensors. Nowadays, the search for more efficient electron transfer between the active site of the enzyme and the electrode surface, in order to infer more sensitivity to the biosensors. In addition the aspects related to the low stability presented by the enzyme with time, temperature and pH, has given an incentive to search modifications in the amperometric biosensor configurations. A new alternative is based on the use of biomimetic chemistry [28,29] and artificial enzymes [30,31] that try to mimic natural enzymes with the same effectiveness and selectivity, and they can be used to construct amperometric sensor with higher sensitivity. In these devices, a redox substance may be immobilized on the electrode surface and work as an active center of the

* Corresponding author. Tel.: +55 19 3521 3053; fax: +55 19 3521 3023.
E-mail address: gushikem@iqm.unicamp.br (Y. Gushikem).

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enzyme that catalyzes the substrate conversion in the same way. This concept has reported in the literature [21–23,32–35] but still presents a great field to be exploited.

In this work we report the in situ generation of copper(II)phthalocyanine (CuPc) in the pores of a matrix SiO_2/C prepared by sol–gel method according to the previously described method [8]. The material obtained, SiO_2/C/CuPc, pressed in a disk format was used to fabricate an electrode and applied as a biomimetic catalyst for the oxidation of dopamine.

2. Experimental

2.1. Reagents

All the reagents used in this work were of analytical grade purity: tetraethyl orthosilicate, TEOS (Sigma–Aldrich, 98%), HF (Vetec, 48%), graphite (Aldrich, 99.99%), HNO_3 (Nuclear, 70%), Tris (hydroxymethyl) aminomethane (Aldrich, 99.9%), dopamine (Sigma), resorcinol (Acros, 98%), catechol (Acros, 99%), H_3PO_4 (Nuclear, 85%), H_3BO_3 (Merck, 99.8%), acetic acid (Nuclear, 99.9%), KCl (Vetec, 99%). Other used reagents were: ethanol (99.9%); physiological solution (Arboeto) and HCl (37%, Synth).

2.2. Preparation of material

2.2.1. Preparation of the SiO_2/C by the sol–gel method

The SiO_2/C matrix was that prepared by the sol–gel processing method, according to the procedure [8]: briefly, 4 mL of deionized H_2O and 0.1 mL of concentrated HNO_3 were added to 50 mL of a solution of tetraethylorthosilicate and absolute ethanol in the proportion 1:1 (v/v) of TEOS/ethanol. The resulting solution was heated to reflux temperature for 3 h under continuous stirring (solution A). Solution A was cooled to room temperature and then under continuous stirring 4.0 mL of deionized water and 50 wt% graphite, calculated from the expected SiO_2 weight, was added. To this mixture 0.5 mL of HF was added and then sonicated until gelation of the material, which occurred about 30 min after adding HF. The resulting material was stored in the hood for a week at room temperature for solvent evaporation. The material obtained in the powder form was immersed in 50 mL of 2.0 mmol L^{-1} HCl and stirred for 30 min, then filtered and washed with deionized water. Finally it was washed with absolute ethanol in a Soxhlet extractor for 3 h, and the solvent was eliminated under vacuum (0.13 Pa), at 393 K. The materials obtained, containing 50 wt% graphite, will hereafter be designated as SiO_2/50 wt% C.

2.2.2. In situ synthesis of Cu(II)phthalocyanine in the pores of the matrix

CuPc was synthesized in situ on the SiO_2/50 wt% C powder matrix as described elsewhere for a similar material [36]. In brief, 1.0 g of SiO_2/C was immersed in 10 mL of 0.01 mol dm^{-3} copper acetate, $Cu(OAc)_2$, and the mixture was heated in a water bath at 343 K until complete evaporation of the solvent. The dry solid, now represented as SiO_2/C/Cu(II), was mixed with 0.22 g of phthalonitrile and heated in an ampoule at 493 K for 3 h to form the CuPc complex. Copper phthalocyanine not confined in the matrix pores and unreacted phthalonitrile were removed from the solid surface in a Soxhlet extractor with absolute ethanol. Then the solid was heated at 398 K under vacuum to evaporate all the solvent.

2.3. Characterization of the material

Specific surface area (S_{BET}) was determined by the BET multipoint technique and the average pore diameters were obtained from the sorption–desorption isotherms by the BJH method. The measurements were carried out on an Autosorb 1 Quantachrome instrument with the materials previously degassed at 423 K for 19 h, before analyzing.

The electronic spectrum of CuPc prepared in situ on the SiO_2/C matrix was obtained using the diffuse reflectance technique on a UV–vis DRS CARY 5G UV/vis spectrophotometer. Barium sulphate was used as the white reference sample. The Kubelka–Munk function was used for the analysis of diffuse reflectance spectrum.

2.4. Electrode preparation and amperometric measurements

The working electrode was prepared by pressing 25 mg of SiO_2/C/CuPc under a pressure of 4 ton, at normal atmospheric conditions. The resultant disk of geometric area (0.20 cm^2) was immersed in pure melted paraffin at 343 K under vacuum (0.13 Pa), until all adsorbed gas in the matrix pores was completely eliminated. The resulting self-supported disk was polished with emery paper to remove the paraffin from the disk surface, and then glued with cyanoacrylate ester glue to the end of a glass tube (external area of 0.20 cm^2 and 15 cm length). A copper wire linked to the disk by graphite powder inserted inside the tube made the electrical contact.

Amperometric measurements were carried out with a PGSTAT-20 (Autolab) potentiostat–galvanostat using an electrochemical cell with three electrodes at room temperature. A saturated calomel electrode (SCE) and Pt wire were used as reference and auxiliary electrode, respectively. The pressed disk of SiO_2/C/CuPc was used as a working electrode. The measurements were carried out using the electrochemical cell containing 25 mL of Britton Robinson buffer (BRB) solution containing 1 mol dm^{-3} KCl. The experiments to find the optimum operational conditions for the biomimetic biosensors were carried out using dopamine. An adequate potential was applied in this system and the current was continuously monitored until reach the steady state. Then, hydrogen peroxide solution was added to the buffer solution monitoring the current for several seconds (until reach the steady state). After that, successive additions of standard solutions of the dopamine were done every 100 s.

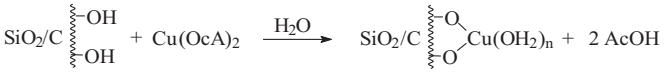
3. Results and discussion

3.1. Characteristics of the SiO_2/C matrix

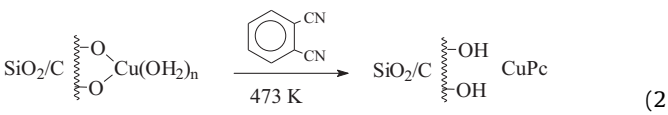
The adsorption–desorption nitrogen isotherm of the matrix SiO_2/C (data not shown) exhibits the presence of hysteresis, typical of mesoporous materials. The material shows a mesopore distribution region (data not shown) with maximum at 15.8 nm diameter, according to the IUPAC classification [37]. The specific surface area, S_{BET}, and the pore volume, p_v, obtained from the isotherms of the material used to fabricate the electrode are: S_{BET} = 170 m^2 g^{-1} and p_v = 0.90 cm^3 g^{-1}.

3.2. In situ generation of CuPc

The in situ generation of CuPc can be described by two steps reaction. In the first step (Eq. (1)) Cu(II) is adsorbed on the silica surface by a reaction with formation of a Si–O–Cu bond:



(1)



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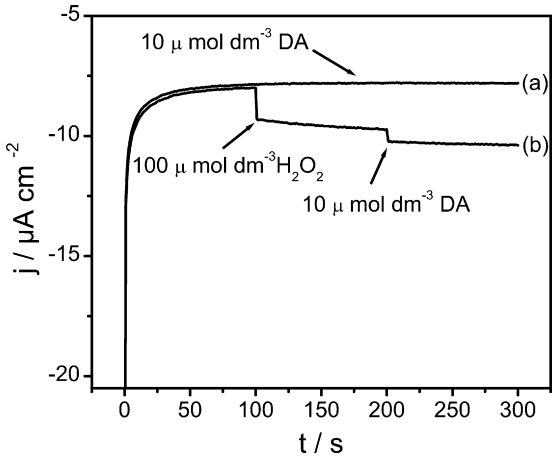

Fig. 1. Signals obtained with the proposed sensor using SiO_2/C/CuPc: (a) in absence and (b) presence of 100 μmol dm^{-3} H_2O_2. Each step corresponds to the increment of 10 μmol dm^{-3} dopamine. The inset figure shows the analytical curve. Applied potential −20 mV vs SCE in 0.08 mol dm^{-3} BRB at pH = 6.0 containing 1 mol dm^{-3} KCl.

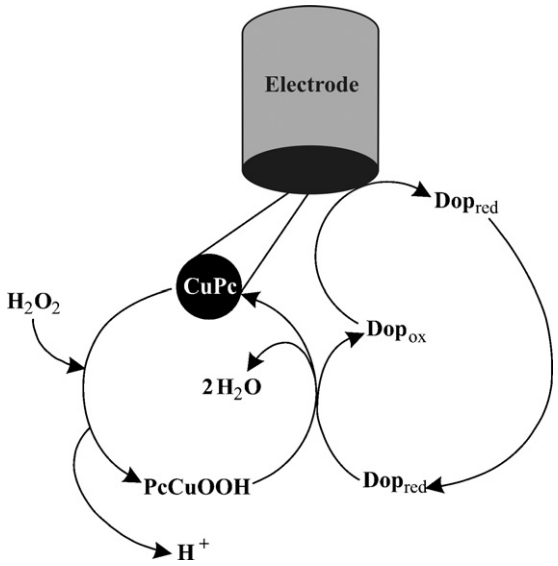

Fig. 2. Proposed mechanism for the sensor SiO_2/C/CuPc response for dopamine. Copper phtalocyanine is represented by $CuPc_{red}$, $CuPc_{ox}$ is oxidized CuPc, and Dop_{red} and Dop_{ox} are the reduced and oxidized dopamine species, respectively.

where –OH represents the Brϕnsted acid groups present on the matrix surface. In the second step the adsorbed Cu(II) served as the template for phthalocyanine complex formation inside the silica pores. The adsorbed Cu(II) on the matrix surface, in the presence of phthalonitrile at 473 K, forms CuPc through the reaction described by Eq. (2).

The UV–vis diffuse reflectance spectrum of the immobilized CuPc on SiO_2/C material, shows two electronic transition peaks observed at 589 and 689 nm and for standard CuPc at 560 and 689 nm. These two transitions are assigned as Q bands for Cu(II) under D_{4h} symmetry, slightly distorted in the CuPc confined in the pores of the matrix [38].

3.3. Electrochemical measurements

3.3.1. Electrode response

A pressed disk of SiO_2/C/CuPc was used to fabricate the electrode to test the potential usefulness of the catalyst to mimic the dopamine monooxygenase. The quantity of electroactive species was estimated from a cyclic voltammetry technique obtained at in 0.08 mol dm^{-3} BRB at pH 6.0 containing 1 mol dm^{-3} KCl, scan rate of 0.005 V s^{-1}, under a nitrogen atmosphere (data not shown). The charge, *Q*, flowing during the oxidation–reduction process of the CuPc was determined by integrating the area under the cyclic voltammetric curve. The amount of electroactive species estimated was 7.3×10^{-8} mol cm^{-2}.

Fig. 1 shows the results obtained in the experiments carried out in the presence and absence of hydrogen peroxide. In the absence of H_2O_2 (curve a), no cathodic currents were observed, which could be attributed to the incapability of the SiO_2/C/CuPc to directly oxidize the dopamine. On the other hand, good cathodic current after adding peroxide and dopamine is observed (curve b in Fig. 1), demonstrating that peroxide plays an important role in the catalytic process.

A higher sensitivity was obtained for H_2O_2 concentration of 200 μmol dm^{-3}, however such higher concentration resulted in poor stability of the electrode. Probably the hydrogen peroxide in high concentration leads to form an inactive form of the catalyst like in enzyme system [23]. Therefore, the use of a minimum amount of hydrogen peroxide in the media is desirable, but it should be sufficient to present high sensitivity. Thus, 100 μmol dm^{-3} hydrogen peroxide allows good sensitivity, without affecting the stability. This concentration was established for further experiments.

Based on these results, a possible mechanism for the sensor response was proposed as schematized in Fig. 2. This mechanism is similar to those proposed for phenolic compound with biomimetic catalysts of dopamine β-monooxigenase [32]. The most important stage for dopamine quantification is the chemical oxidation of dopamine species by the activated PcCu–OOH on the electrode surface, the oxidized dopamine is electrochemically reduced on the electrode surface recycling the substrate, and consequently resulting in signal amplification. The hydrogen peroxide is necessary to activate the CuPc forming an active form PcCu–OOH to oxidize dopamine, which is electrochemically reduced on the electrode surface. One point that should be emphasized is the role of SiO_2 in this material. Copper is mostly adsorbed on SiO_2, which is insulator and thus, the electron transfer between CuPc and electrode is not favored, corroborating that the electrons transfer occur predominately between quinone species and carbon domain of the electrode.

3.3.2. Influence of hydrogen peroxide

In the proposed sensor, the prior addition of hydrogen peroxide, before adding dopamine, increased the sensitivity of the electrode. This fact can be explained based on the catalysis mechanism of the dopamine monooxygenase, very well explained in literature [39–41], which involves the generation of copper-hydroperoxy species (Cu^{II}–O–O–H). In the enzyme, the initial chemical event involves two electron and one proton transfer from the copper sites and an active site with acidic group of the protein, respectively, to oxygen to yield a copper-hydroperoxy intermediate. Cleavage of the O–O bond and hydrogen extraction from the substrate forms water, copper-oxo and substrate radical, which consequently combine to form hydroxylated product. In our case, the hydrogen peroxide addition in the working solution is necessary to form Cu^{II}–O–O–H like in enzyme to be able to oxidize the substrate. On the other hand, the regeneration of the oxidized catecholamines by applying an adequate potential is feasible. On this basis, the mechanism presented in Fig. 2 was proposed for this biomimetic biosensor. Initially, Cu^{2+} in presence of H_2O_2 forms the Cu^{II}–O–O–H species. This species will oxidize dopamine in the catechol ring to form 1,2-quinone. In this stage, that represents the most important step for dopamine quantification, occurs the electrochemical reduction of the quinone species on the electrode surface, through

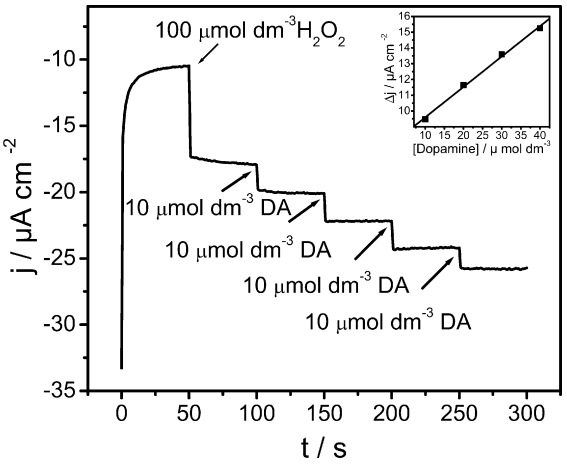

Fig. 3. Amperometric response for the biomimetic biosensor for dopamine. Each step corresponds to the increment of 10 μmol dm^{-3} dopamine and containing 100 μmol dm^{-3}. The inset figure shows the analytical curve. Applied potential −20 mV vs SCE in 0.08 mol dm^{-3} BRB at pH = 6.0 containing 1 mol dm^{-3} KCl.

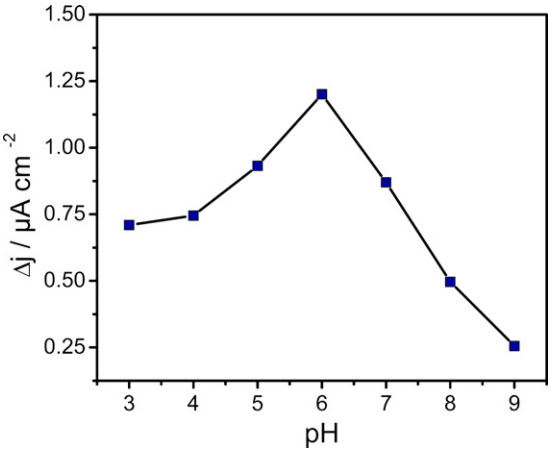

Fig. 5. Influence of the pH on the current density Δ*j*. Measurements carried out in 0.08 mol dm^{-3} BRB containing 1 mol dm^{-3} KCl, and 10 μmol dm^{-3} of dopamine and 100 μmol dm^{-3} of H_2O_2.

the application of a suitable potential. This mechanism also explains the high sensitivity of the sensor by the signal amplification due to the cyclic reaction [42,43]. Fig. 3 shows the prior addition of H_2O_2 to the solution before adding dopamine and shows a very good sensitivity of the electrode. It corroborates the proposed mechanism as depicted in Fig. 2.

3.3.3. *Influences of the applied potential, buffer and solutions pH*

In order to establish the optimized conditions for amperometric measurements, the influence of the applied potential, buffer solution and pH were also investigated and the best sensor responses were obtained at −20 mV vs SCE at pH = 6 (Fig. 4). It can be seen that the current density referring to dopamine reduction increases from *E* = −80 up to maximum at −20 mV and then decrease up to 80 mV. This behavior has been described as a competitive mechanism for copper electro-reduction (at about −40 mV and 0 mV vs SCE), which can result in a low number of active sites of oxidized copper species ($CuPc_{ox}$) promoting a decrease in the efficiency of dopamine oxidation by the chemical route (as depicted in Fig. 3). To determine the influence of different buffers on the electrode response for dopamine measurements were carried out in 0.08 mol dm^{-3} buffers (BRB, HCl/KOH and Tris) at pH = 6.0 in the presence of 100 μmol dm^{-3} H_2O_2 and 10 μmol dm^{-3} of dopamine, at applied potential of −20 mV vs SCE. The results obtained for current intensity changes, Δ*j*/μA cm^{-2}, for BRB = 1.76, HCl/KOH = 1.56 and Tris = 1.42 are indicating that the influence of the buffers used does not significantly affect the electrode response.

In the study carried out to determine the influence of the BRB concentration on the sensor response for dopamine was also checked. The results showed that practically the same responses were obtained in the concentration range from 0.02 up to 0.12 mol dm^{-3}. Thus, the best response was obtained at 0.08 mol dm^{-3} and thus selected for further experiments.

The investigation to evaluate the pH effect on the sensor response showed an optimum pH of 6.0 (Fig. 5) in 0.08 mol dm^{-3}. At lower pH the formation of the Cu–OOH is minimized according to the mechanism. Decreasing the formation of the active site (Cu–OOH) the sensitivity will be also decreased. In addition dopamine will be protonated at lower pH making difficult the interaction with the metal center. For Higher pH than 6 is favored to form CuOH that is not active and decreasing the sensitivity.

3.3.4. *Sensor characteristics*

Under optimized conditions, the proposed sensor showed a linear response range for dopamine concentration, varying from 10 up to 140 μmol dm^{-3} with a sensitivity of 0.63 nA dm^3 μmol^{-1} cm^{-2} (Fig. 6), and expressed by the equation:

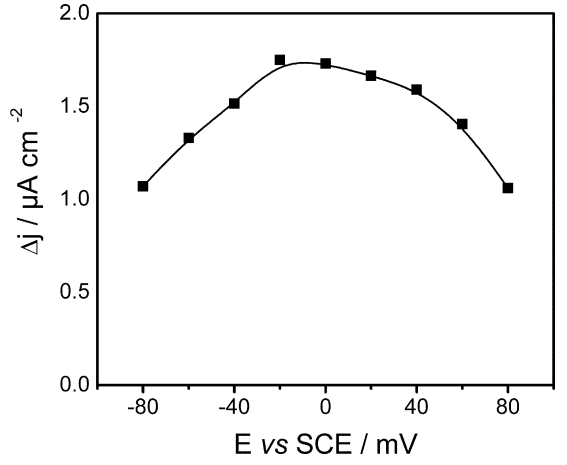

Fig. 4. Influence of the applied potential on the current density Δ*j*. Measurements carried out in 0.08 mol dm^{-3} BRB at pH = 6.0 containing 1 mol dm^{-3} KCl, and 10 μmol dm^{-3} of dopamine and 100 μmol dm^{-3} of H_2O_2.

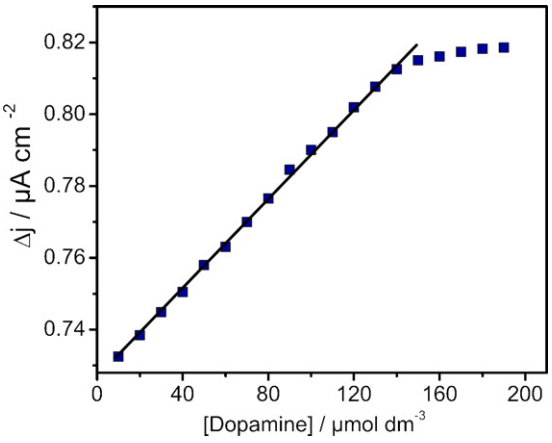

Fig. 6. A typical profile of the sensor response using the optimized conditions. Applied potential of −20 mV vs SCE, in 0.08 mol dm^{-3} BRB at pH = 6.0 containing 1 mol dm^{-3} KCl, and 100 μmol dm^{-3} of H_2O_2.

Table 1
Analytical parameters for dopamine detection with biomimetic sensors under optimized amperometric conditions.

Biomimetic sensor	Dynamic range/(μmol dm^{-3})	LOD (μmol dm^{-3})	Sensitivity (nA dm^3 μmol^{-1} cm^{-2})	Ref.
Th^{IV}-HCF[a]	8–2000	4.7	–	[46]
Fe^{III}T4MpyP-His[b]	0.6–6.0	0.35	0.061	[21]
$[Cu(bipy)_2]Cl_2$[c]·$6H_2O$	35–240	8.0	2.02	[47]
Ag/CCE[d]	6.6–120	1.4	26.30	[48]
RuO_2/MWNT[e]	0.6–360	0.06	0.084	[49]
SiO_2/C/CuPc	10–140	0.60	0.63	This work

[a] Thorium (IV)-hexacyanoferrate.
[b] Iron tetra-(N-methyl-4-pyridyl)porphyrin-histidine.
[c] Bis(2,2′-bipyridil) copper chloride.
[d] Silver Ceramic composite electrode.
[e] Multiwalled carbon nanotubes.

$$\Delta j/\text{nA cm}^{-2} = 0.141\ (\pm 0.491) + 0.628\ (\pm 0.006)\ [\text{Dopamine}]/\mu\text{mol dm}^{-3}$$

with a correlation coefficient of 0.999 for $n = 14$.

The limit of detection (3 times standard deviation of the blank divided by the slope of calibration curve), LOD = 0.62 μmol dm^{-3} was found. In addition, considering the time to reach 100% of the signal, the response time was about 1 s, which is better than the response times of other sensors presented in the literature for phenolic compounds [23,44,45].

The repeatability in the measurements was evaluated through 10 successive experiments carried out with 10 μmol dm^{-3} dopamine solution. The repeatability data in the electrode preparation were calculated in term of relative standard deviation of 38% for five preparation, thus the preparation of different electrodes present a good variation because the difficulty to reproduce the surface area of the electrode. However, if we use the same electrode we can verify the great stability and repeatability of the measurement with the same electrode with a RSD of 1.37% (for $n = 10$). The lifetime of the sensor was more than 9 months, stored at room temperature and there is no significant decrease in the sensitivity of the sensor was observed (data not shown).

A comparison of the analytical parameters for dopamine with those previously reported for other biomimetic systems, [21,46–49], under similar experimental conditions, is presented in Table 1. A low detection limit and a higher sensitivity are observed, even when compared to biosensors based on peroxidase or tyrosinase enzymes [44,50] for phenol determinations. Such good analytical responses can be attributed to the efficiency of the reaction between the peroxide and SiO_2/C/CuPc (biomimetic catalyst) and also SiO_2/C/PcCuOOH with dopamine as well as the electrons transfer from quinone to electrode surface.

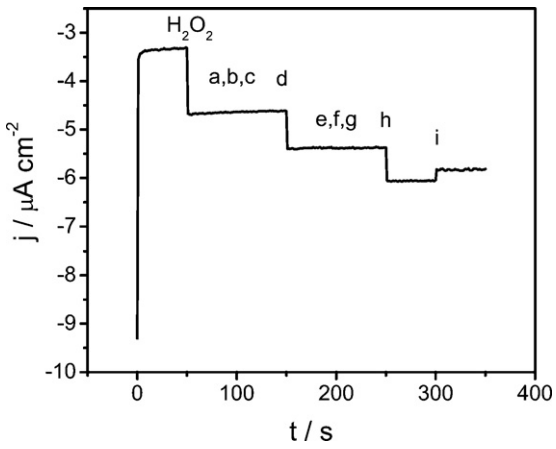

Fig. 7. Current *i* vs time for the addition of catechol (CA) resorcinol (RE) ascorbic acid (AA) and DA into the electrochemical cell in sequence at 75, 150, 175, 250 and 300 s. Concentrations (in μmol dm^{-3}) of the analytes in the reaction cell: (a) [CA] = 10, (b) [RE] = 10; (c) [AA] = 2; (d) [DA] = 10 (e) [CA] = 20 (f) [RE] = 20 (g) [AA] = 4 (h) [DA] = 20 and (i) [AA] = 5. Applied potential of −20 mV vs SCE, in 0.08 mol dm^{-3} BRB at pH = 6.0 containing 1 mol dm^{-3} KCl, and 100 μmol dm^{-3} H_2O_2.

3.3.5. *Sensor application: interference and determination of dopamine in physiological solution*

The sensor response was tested in the presence of 10 μmol dm^{-3} dopamine and interfering compounds such as catechol, resorcinol and ascorbic acid. It can be seen in Fig. 7 that there is no interference with catechol and resorcinol even in the same concentration with dopamine and only ascorbic acid gave a negative interference from concentrations higher than 4.0 μmol dm^{-3}. This behavior can be assigned to the reaction between ascorbic acid and hydrogen peroxide, decreasing the formation of the copper hydroperoxy sites.

In order to evaluate the sensors applicability, dopamine was determined in a sample. A known concentration of dopamine solution was made in the physiological solution (0.9%, m/v) and also physiological solution was used as supporting electrolyte. The sensor gives a very good response for dopamine determination in this solution. The recovery data about 100 (±2)% was obtained using standard addition method (data not shown).

4. Conclusions

The proposed enzymeless biosensor, as a SiO_2/C/CuPc, showed a wide response range (10–140 μmol dm^{-3}), high sensitivity of 0.63 nA dm^3 μmol^{-1} cm^{-2} and with a detection limit of 0.6 μmol dm^{-3} of dopamine. This sensor showed a long lifetime of 9 months, great stability and repeatability and a short response time of (1 s) for determination of dopamine. The proposed sensor was better than the most of conventional biosensors (based on enzyme) and other enzymeless biosensors described in the literature. These characteristics can be assigned to the conductivity of the material and the environment of the copper complex in the porous material keeping the great reactivity after activating it with hydrogen peroxide. The proposed sensor is highly selective for dopamine determination; it does not show any interference with other phenolic compounds. Indeed, this sensor was successful employed for determination of dopamine in sample.

In this sense, this work depicts that the development of biomimetic biosensors is a promising subject, since simple stable molecules can be used to catalyze redox reaction of extremely important analytes like dopamine.

Acknowledgements

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