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Development of microelectrode arrays modified with inorganic-organic composite materials for dopamine electroanalysis

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ABSTRACT

New electrode materials based on composite inorganic redox material-organic conducting polymer for electroanalysis of dopamine were developed. The composite inorganic-organic coatings based on Prussian blue (PB) and poly(3,4-ethylenedioxythiophene) (PEDOT) have been prepared by electrochemical methods onto gold disk microelectrode arrays. Both insoluble and soluble forms of PB were prepared in situ inside the organic matrix and their electrochemical behaviour was investigated in electrolyte solution. The composite inorganic-organic coating containing the soluble PB form exhibited good electrocatalytic activity towards dopamine (DA) oxidation in aqueous buffered solutions. The DA concentration was determined by cyclic voltammetry in the presence of a high excess of ascorbic acid (AA). A linear response for DA concentrations ranging from 10 µM to 50 µM, in the presence of 1 mM AA, with a sensitivity of 460 µA/µM and a detection limit of 4.3 µM, have been obtained.

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1. Introduction

37 Electrochemical sensors and biosensors for the electroanalysis of biologically active compounds have attracted a great deal of 38 interest due to their analytical performance. Electrochemical sen-39 sors provide low detection limits, a wide linear response range, 40 and good stability and reproducibility, among other advantages. 41 However, bare electrodes are more likely than chemically modified 42 electrodes to suffer from interferences or surface fouling by prod-43 ucts arising from follow-up reactions, associated to the main elec-44 trochemical process. The modification of electrode surfaces with 45 46 inorganic or organic coatings often avoids these drawbacks and represents a rapid and versatile resource for the preparation of sta-47 ble and selective new electrochemical sensors [1-5]. Inorganic 48 coatings consisting of transition metal hexacyanoferrates, such as 49 Prussian blue (PB, ferric ferrocyanide $Fe_4^{III}[Fe^{II}(CN)_6]_3$), have been 50 51 used in the preparation of electrochemical sensors as well as amperometric biosensors [6-10]. PB is a mixed-valence compound 52 53 that can be deposited onto the electrode surface as an electroactive film. There are two forms of PB that have been called "water insol-54 uble PB", $Fe_4^{III}[Fe^{II}(CN)_6]_3$, and "water soluble PB", $KFe^{III}[Fe^{II}(CN)_6]_6$, 55 respectively [11]. The soluble form of PB forms in the presence of 56

an excess of potassium ions. The reduction of PB yields a colorless compound called Everitt's Salt (ES), while the oxidation of PB gives Berlin Green (BG). Pt/PB modified electrodes typically display two redox waves at ca. 0.2 V and 0.9 V vs. SCE, respectively. These waves correspond to the reduction of PB to ES and to the oxidation of PB to BG, respectively. These redox processes can be described by using the two formula of PB, i.e. the soluble form (Eqs. (1) and (3)) and the insoluble form (Eqs. (2) and (4)), respectively, according to the following reactions [11,12]:

- redox wave corresponding to the PB/ES system:
- $KFe^{II}[Fe^{II}(CN)_6] + e^- + K^+ \iff K_2Fe^{II}[Fe^{II}(CN)_6] \tag{1}$

$$Fe_4^{III}[Fe^{II}(CN)_6]_3 + 4e^- + 4K^+ \iff K_4 Fe_4^{II}[Fe^{II}(CN)_6]_3$$
(2)

• redox wave corresponding to the PB/BG system:

$$KFe^{III}[Fe^{II}(CN)_6] - e^- - K^+ \iff Fe^{III}[Fe^{III}(CN)_6]$$
(3)

$$Fe_4^{III}[Fe^{II}(CN)_6]_3 - 3e^- + 3Cl^- \iff Fe_4^{III}[Fe^{III}(CN)_6Cl]_3$$
(4)

Conducting polymers such as polypyrrole, polyaniline, polythiophene, and their derivatives, have been also used for the construction of electrochemical sensors based on modified electrodes. The preparation of composite inorganic-organic coatings capable of 23

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89 fast bulk and interfacial electron transfer during redox reactions is 90 a method of choice for the construction of analytical devices. Var-91 ious procedures for the preparation of inorganic-organic compos-92 ite material coatings have been recently reported [13]. Composite 93 inorganic-organic coatings containing transition metal hexacyano-94 ferrates and conducting polymers have been prepared in various 95 configurations on electrode surfaces [14-17]. It has been demon-96 strated that the inorganic compound acts as a redox mediator, 97 while the organic component plays the role of a stable matrix or 98 a permselective membrane. By this approach, most stable, highly 99 conducting, and selective coatings can be easily deposited over 100 electrode surfaces. The choice of these components for the preparation of the composite materials is based on their unique proper-101 ties, i.e. the excellent stability of the PEDOT layer in aqueous 102 103 solution and its doped state [18-20], and the electrocatalytic activ-104 ity of PB [21–23]. The electrochemical redox properties of each 105 component are expected to produce a synergistic effect, taking into 106 consideration that the PEDOT layer is in its conducting state in the 107 potential region were the PB redox mediator displays good electro-108 catalytic activity.

109 This work reports the preparation of new electrode materials 110 consisting of PB and poly(3,4-ethylenedioxythiophene) (PEDOT) deposited as thin films on gold disc microelectrode arrays is re-111 ported. We modified disk microelectrode arrays with two compos-112 113 ite organic-inorganic materials, based on the soluble and the 114 insoluble forms of PB in situ inside a PEDOT matrix. We then inves-115 tigated the oxidation of DA at these modified microelectrode arrays 116 by cyclic voltammetry (CV).

117 2. Experimental

118 2.1. Chemicals

All chemicals were used as received without any further purification. 3,4-ethylenedioxythiophene (EDOT, Aldrich) was used for
the electrochemical preparation of the corresponding polymer.
Distilled water was always used to prepare aqueous solutions.

123 2.2. Electrochemical measurements

124 The electrochemical experiments were carried out with an 125 Autolab potentiostat/galvanostat 302 N (Ecochemie, The Nether-126 lands) coupled to a PC running the GPES software, using a single-127 compartment cell with three electrodes, at room temperature. 128 The electrodes used were: a gold disk microelectrode array as 129 working electrode, a saturated calomel electrode, SCE, as a refer-130 ence electrode (Metrohm), and a platinum wire (Metrohm) as aux-131 iliary electrode. Before each electrochemical measurement the 132 surface of the working microelectrode array was electrochemically 133 activated in 0.1 M KCl aqueous solution by holding the electrode potential at 0.0 V for 10 s followed by a second potential step at 134 -2.0 V for 10 s. These potential steps were applied twice to acti-135 vate the microelectrode arrays. The cyclic voltammograms were 136 137 recorded simultaneously at both microelectrode arrays, using the 138 BIPOT module of the potentiostat. The solutions were bubbled with high purity argon and a flow of argon was maintained over the 139 140 solution during the measurements.

141 2.3. Deposition procedure of PEDOT–PB composite films

142 The composite inorganic–organic coatings, i.e. PEDOT–PB-s and 143 PEDOT–PB-i, respectively, have been prepared by a two-step meth-144 od. For both coatings, the PEDOT layer was first electrogenerated 145 from an aqueous solution containing 0.01 M EDOT and 0.1 M 146 K_3 [Fe(CN)₆] as supporting electrolyte by potential cycling in the potential range from open circuit potential, OCP, to +1.0 V and re-147 versed back to -0.6 V, at a scan rate of 0.05 V s $^{-1}$ for five consecu-148 tive scans. The modified electrode obtained in the first step is 149 referred to as Au/PEDOT-FeCN. In the second step, the Au/PED-150 OT-FeCN modified electrode was immersed in 2 M FeCl₃, 0.1 M 151 KCl and 0.01 M HCl aqueous solution and the electrode potential 152 was scanned from 0.6 to -0.2 V at a scan rate of 0.05 V s $^{-1}$ for five 153 successive scans. The soluble PB is formed inside the PEDOT matrix 154 during this potential cycling. The resulting modified electrode is 155 denominated Au/PEDOT-PB-s. The composite coating containing 156 the insoluble form of PB was prepared in a similar manner, except 157 that Na₄[Fe(CN)₆] was used as supporting electrolyte in the first 158 deposition step, and no KCl was used in the second step. The ab-159 sence of the potassium ions in these deposition solutions results 160 in the formation of the insoluble form of PB. The resulting modified 161 electrode is referred as to Au/PEDOT-PB-i. 162

2.4. Fabrication of microelectrode arrays

The microelectrode arrays used in this work comprise 816 164 microelectrodes of 10 μ M radius. They are arranged in a 24×34 165 square lattice and present a centre-to-centre separation of 50 µM 166 along both the x and y axes. These microelectrode arrays were fab-167 ricated on silicon chips using standard microfabrication tech-168 niques, as described in previous works [24], but a short summary 169 will be given here for convenience. After growing a $1 \mu M$ thick 170 layer of thermal oxide over a silicon wafer, a triple metal layer con-171 sisting of Ti (25 nm), Ni (25 nm) and Au (100 nm) is deposited. The 172 gold areas where the microelectrodes and the contacts will be de-173 fined are etched in a wet step following a photolithographic step. 174 This photolithographic step was performed insolating a positive re-175 sist (Clariant AZ6512) through a suitable dark field mask. After the 176 metal has been etched, the excess resin is stripped in acetone and 177 the wafers are thoroughly rinsed. Next a passivation layer is depos-178 ited over the wafers to protect the connection pads and also to help 179 define the final geometry of the devices. This passivation layer is a 180 mixed layer of silicon oxide (700 nm) and silicon nitride (400 nm). 181 The contact pads and the microelectrodes are open through this 182 passivation layer by reactive ion etching after a second photolitho-183 graphic step. Once the contacts are open and the microelectrodes 184 have been defined, the excess resin is stripped and the wafers 185 rinsed. The wafers are then diced into individual chips and 186 mounted on suitable printed circuit boards, where they are wire 187 bonded and encapsulated. 188

3. Results and discussion

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3.1. Preparation and characterization of microelectrode array modified with <u>PEDOT-PB-soluble</u> composite films

Microelectrode arrays were activated according to the procedure described in the Experimental section and then were characterized in aqueous solution containing a redox probe. Fig. 1 shows typical cyclic voltammograms recorded at two microelectrode arrays on a chip in 1 mM K₃Fe(CN)₆ and 0.1 M KCl aqueous solution at a potential scan rate of 0.05 V s⁻¹. From the voltammograms, a population of active microdiscs around 50% was determined. This low yield was due to an imperfect etching of the silicon oxide layer used to pattern the electrodes during their fabrication.

Peak-shaped voltammograms were obtained due to the heavy overlap of the diffusion layers of neighbouring electrodes within the array at the potential scan rate used for voltammetric measurements. The voltammograms are very reproducible, attesting that the arrays behave similarly under these experimental conditions. Once the array was activated and its proper functioning checked,

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Fig. 1. Cyclic voltammograms recorded at the two bare Au microdisk electrode arrays in one chip (dotted and solid line) in 1 mM K_3 Fe(CN)₆ and 0.1 M KCl aqueous solution at a potential scan rate of 0.05 V s⁻¹.

one of the arrays was covered with a pure PEDOT organic coating 207 208 (see Fig. 2A) while the other array was modified with the PED-209 OT-FeCN composite coating (see Fig. 2B). Fig. 2A shows that the polymerisation of PEDOT occurs in the potential range from 0.75 210 211 to 1.0 V ys. SCE, and that the PEDOT layer grows on the electrode 212 surface. The shape of the cyclic voltammograms is similar to that 213 of those recorded on conventional size electrodes and microelec-214 trodes [25,26].

The presence of the inorganic redox mediator results in a peakshaped voltammogram (see Fig. 2B). The electrochemical polymerisation occurs in the presence of ferricyanide ions and thus the resulting organic polymer is doped with counterions from the electrolyte solution.

After the deposition of <u>PEDOT–FeCN</u> coating, the modified electrode array was immersed in Fe³⁺ containing solution in order to prepare the "soluble" PB layer. Fig. 2C reports the cyclic voltammograms recorded at <u>Au/PEDOT–FeCN</u> modified electrode in aqueous solution containing 0.002 M FeCl₃, 0.1 M KCl and 0.01 M HCl.

Note the presence of a redox wave characterized by an anodic peak at ca. +0.3 V and a cathodic peak at ca. +0.27 V, respectively. This redox wave is ascribed to the PB/ES redox system and it is very stable as it can be seen from cyclic voltammograms recorded for five potential scans. Thus the in situ formation of the soluble form of PB is clearly demonstrated. This modified electrode was then immersed in phosphate buffer solution (PBS) and characterized by cyclic voltammetry (see Fig. 3A). The composite coating is very stable in neutral buffered aqueous solution. This is in contrast to PB-only films, which rapidly decompose in such media, Fig. 3B shows the cyclic voltammogram recorded at the "reference" Au/ PEDOT modified microelectrode array from the chip. From Fig. 3B it can be observed a redox wave at ca. +0.15 V that is ascribed to the polaron formation and the corresponding doping-dedoping redox processes. The stability of this wave is similar to those recorded on microelectrode disks and it is more visible than in the case of conventional size electrodes in such buffered solutions. The modified array was further characterized in array mode in a potassium phosphate buffer solution (PBS) and the corresponding voltammograms are depicted in Fig. 3C. It is important to note the successful modification of each electrode in the array as well as their electrochemical behaviour in the absence of the analyte. As to the polaron peak in the PEDOT coating, these measurements



Fig. 2. Cyclic voltammograms recorded at Au disk microelectrode array during the polymerisation of EDOT in 0.01 M EDOT and 0.1 M LiClO₄ aqueous solution (A) and Au electrode during the polymerisation of EDOT in aqueous solution containing 0.01 M EDOT and 0.1 M K₃Fe(CN)₆ (B). Potential scan rate: 0.05 V s^{-1} . The first five consecutive scans are depicted. Inset: the region of electrode potential values where the polymerisation of EDOT takes place. Solid arrows indicate the forward scan. The resulted modified electrodes are referred to as Au/PEDOT (A) and Au/PEDOT–FeCN (B), respectively. (C) Cyclic voltammograms recorded at Au/PEDOT–FeCN modified electrode in aqueous solution containing 2 mM FeCl₃, 0.1 M KCl and 0.01 M HCl during in situ formation of "soluble" PB inside PEDOT matrix. The first five consecutive scans are depicted. Potential scan are electrode is denoted as Au/PEDOT–Ps.

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Fig. 3. Cyclic voltammograms of Au/PEDOT–PB-soluble (A) and Au/PEDOT (B) modified electrodes in 0.1 M potassium phosphate buffer aqueous solution of pH 7.2. Potential scan rate: 0.05 V s^{-1} . The first and the fifth scans are shown. (C) Cyclic voltammograms recorded in array mode with the BIPOT module at Au/PEDOT–PB-soluble (solid line) and Au/PEDOT (dotted line) modified microelectrode array in 0.1 M PBS (pH = 7.2). Potential scan rate: 0.05 V s^{-1} . The electrode potential of the Au/PEDOT modified array follows that of the array modified with the Au/PEDOT–PB-soluble layer.

248 clearly indicate a slight shift of the polaron wave towards more po-249 sitive values in the case of the PEDOT-PB composite coating. More-250 over, the cyclic voltammograms show that the presence of the 251 inorganic redox material increases the conductivity of the coating, 252 i.e. there is a less capacitive like shape for the PEDOT-PB corresponding cyclic voltammograms. The electrochemical redox prop-253 erties of the composite material are mainly dominated by the 254 inorganic redox mediator. In the investigated potential range, the 255 256 PEDOT coating is in its conducting state and it is porous enough to permit the flux of potassium ions, necessary to maintain the 257 258 electroneutrality and to afford the proper redox functioning of 259 the PB component. The positively charged PEDOT matrix facilitates 260 the incorporation of the negatively charged inorganic component 261 PB and assures the excellent stability of the composite material 262 in aqueous buffered solution. These electrochemical properties of 263 the composite materials result in cyclic voltammograms that clearly show the contribution of each component to the overall 264 265 behaviour of the coating.

3.2. Preparation and characterization of microelectrode array modified with <u>PEDOT-PB-insoluble</u> composite films

The preparation and the electrochemical characterization of 268 269 PEDOT-PB-insoluble composite coating deposited as thin film onto 270 Au disk microelectrode arrays were also studied. Fig. 4A shows cyc-271 lic voltammograms recorded at one of the Au electrodes in the chip 272 during the electrochemical polymerisation of EDOT in the presence 273 of sodium ferrocyanide. This redox mediator was chosen to avoid 274 the presence of potassium ions during the preparation of the com-275 posite coating.

There is a small increase of current in the potential range be-276 tween 0.75 and 1.0 V vs. SCE due to the electrochemical polymer-277 isation of EDOT. The presence of the inorganic redox mediator 278 results in a peak-shaped voltammogram. During the electrochem-279 ical polymerisation of EDOT, the ferrocyanide ions are incorporated 280 into the organic matrix. The resulting modified electrode is re-281 ferred as to Au/PEDOT-FeCN-Na. This is the basis for the prepara-282 tion of insoluble PB form. The second microelectrode array was 283 used as substrate for the electrochemical deposition of pure PEDOT 284 layer, and was considered as "reference" coating with respect to 285 the composite one. The shape of the CVs is similar to those pre-286 sented in Fig. 2A. Also, the current increases in the potential range 287 0.75–1.0 V due to the deposition of the PEDOT layer. This modified 288 array is referred to as Au/PEDOT. After the deposition of the PED-289 OT-FeCN-Na coating, the Au/PEDOT-FeCN-Na electrode was im-290 mersed in Fe³⁺ containing aqueous solution so that the insoluble 291 form of PB may form inside the PEDOT matrix (see Fig. 4B). In this 292 case there is no redox wave associated with the PB/ES redox sys-293 tem due to the absence of the potassium ions in both the deposi-294 tion solution and the transfer solution. It is well known that the 295 PB/ES redox wave is evidenced only in potassium containing aque-296 ous solution [12]. This modified electrode is referred as to Au/PED-297 OT-PB-insoluble. This Au/PEDOT-PB-insoluble modified elèctrode 298 was then characterized in sodium phosphate buffer aqueous solu-299 tion. The voltammograms in Fig. 4C (solid line) lack the redox wave 300 characteristic to the PB/ES redox system because potassium ions 301 were absent from the preparation and characterization solutions. 302 As to the "reference" modified electrode, Fig. 4C (dotted line) 303 shows that the electrochemical polymerisation of EDOT was suc-304 cessful, because the redox wave corresponding to the polaron for-305 mation is visible. Next, the Au/PEDOT-PB-insoluble modified 306

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Fig. 4. (A) Cyclic voltammograms recorded at Au microelectrode array in aqueous solution containing 0.01 M EDOT and 0.1 M Na₄Fe(CN)₆. Potential scan rate: 0.05 V s⁻¹. The first five consecutive scans are depicted. (B) Cyclic voltammograms recorded at Au/PEDOT–FeCN–Na array in aqueous solution containing 2 mM FeCl₃, and 0.01 M HCl. Potential scan rate: 0.05 V s⁻¹. The first five scans are represented. (C) Cyclic voltammograms recorded at Au/PEDOT–PB-insoluble (dotted line) and Au/PEDOT (solid line) modified electrodes in 0.1 M sodium phosphate buffer solution. (D) The first five scans recorded at Au/PEDOT–PB-insoluble modified electrode in potassium phosphate buffer solution of pH = 7.2. Potential scan rate: 0.05 V s⁻¹.

307 electrode was immersed in 0.1 M potassium phosphate buffer aqueous solution and investigated by CV (see Fig. 4D). Note that 308 309 presence of potassium ions in high concentration does not allow 310 the conversion of the PB insoluble form into the soluble one. However, this conversion is observed in the case of PB only modifying 311 layer and it is not fully reversible once the PB layer has been in con-312 tact with electrolyte solution containing other cations, like Na⁺, Li⁺, 313 314 Cs⁺ [12,27,28]. In our case, a high concentration of sodium ions during the preparation of the composite material may block the 315 316 channels in the zeolitic structure of PB, complicating their later 317 replacement by potassium ions.

318 3.3. Analytical applications of PEDOT–PB-soluble modified array in the 319 voltammetric determination of dopamine (DA)

The modified array was used in the voltammetric determination of DA in neutral buffered aqueous solution. Fig. 5A reports the CVs recorded simultaneously at both microelectrode arrays on a chip.

323 The PEDOT-PB-soluble modified array showed excellent analytical performance in the voltammetric determination of DA. The 324 325 sensors responds to low DA concentrations, i.e. from 2 to $10 \,\mu$ M, by using cyclic voltammetry as detection method, and these low 326 327 DA concentrations can be usually achieved only by using differen-328 tial pulse and square wave voltammetry [10,20]. The sensor 329 showed a linear response according to the equation: i_{pa} (nA) = 1.2 C_{DA} (μ M) + 3.6, with a correlation coefficient of R^2 = 0.9966 330 331 (see inset of Fig. 5A), and a detection limit of 2 µM. Surprisingly, 332 the PEDOT-only coating showed no electrocatalytic activity to-333 wards DA oxidation. Therefore these results clearly demonstrate 334 the benefit of using the PEDOT-PB-soluble modified microelec-

trode array. The voltammetric determination of DA was also per-335 formed in the presence of a strong interferent like ascorbic acid 336 (AA). It is well known that AA strongly influences the voltammetric 337 determination of DA, and therefore we choose to study the electro-338 catalytic efficiency of the composite coating for simultaneous 339 determination of DA in the presence of AA. Fig. 5B reports the cyc-340 lic voltammograms of the PEDOT-PB-soluble modified array re-341 corded during the voltammetric determination of DA in the 342 presence of an excess of 1 mM AA. The DA oxidation produces an 343 anodic wave at 0.28 V, while the AA oxidation occurs at 0.1 V that 344 is a peak potential separation of ca. 180 mV was obtained, as it can 345 be seen from the square wave voltammogram depicted in the inset 346 of Fig. 5B. The large peak potential separation obtained at the mod-347 ified microelectrode array is attributed to the electrostatic interac-348 tion between the analytes and the composite coating. At 349 physiological pH, DA exists as a cation and AA as an anion. The po-350 tential shift towards negative potential values observed for AA oxi-351 dation can be ascribed to the electrostatic interaction of the 352 ascorbate anions with the polarons. It is well known that conduct-353 ing polymers can act as redox mediators and the electrocatalytic 354 activity arises from the formation of polarons, that is of positive 355 charges on the polymer backbone. Therefore, the oxidation of AA 356 is facilitated at PEDOT-modified electrodes by the negative charge 357 of the molecule, while oxidation of positively charged species, like 358 DA, could be made more difficult. On the other hand, the presence 359 of the negatively charged inorganic redox mediator inside the PED-360 OT matrix could influences the oxidation of DA, by reducing the 361 oxidation potential in comparison with an unmodified electrode. 362 Therefore, the electrochemical response of the modified array to-363 wards both analytes can be considered as a result of a synergistic 364



Fig. 5. (A) Cyclic voltammograms recorded at Au/PEDOT-PB-soluble (bottom) and Au/PEDOT (top) modified microelectrode array in 0.1 M PBS containing various DA concentrations: 2, 4, 6, 8, and 10 µM. Potential scan rate: 0.05 V s⁻¹. Inset: the linear dependence of the anodic peak current on DA concentration. (B) Cyclic voltammograms recorded at Au/PEDOT-PB-soluble (bottom) and Au/PEDOT (top) modified microelectrode array in 0.1 M PBS containing various DA concentrations: 10, 20, 30, 40, and 50 µM, in the presence of 1 mM AA. Potential scan rate: 0.05 V s⁻¹. Insets: the linear dependence of the anodic peak current on DA concentration (left upper side) and the square wave voltammogram recorded at the modified electrode in 0.1 M PBS containing 50 µM DA and 1 mM AA; step potential 0.01 V, amplitude 0.025 V, frequency 10 Hz (right lower side)

behaviour of the organic and inorganic components of the compos-365 ite material. The oxidation of DA at this modified electrode is 366 reversible, while AA oxidation is irreversible as it can be seen from 367 Fig. 5A. The shift of peak potentials towards negative values attests 368 the electrocatalytic activity of the composite material. The inor-369 370 ganic redox mediator, i.e. PB, is able to mediate the oxidation of 371 DA at the same potential values corresponding to the PB/ES redox 372 system. In the same time, the polarons from the PEDOT matrix are 373 able to mediate the oxidation of AA and to assure the peak poten-374 tial separation between the anodic waves of the analytes. This 375 behaviour is based on the electrochemical properties of the com-376 posite materials, which combine the excellent stability of PEDOT 377 in aqueous solution and its permselective membrane like behav-378 iour with the good electrocatalytic activity of PB. The choice of 379 these components in the fabrication of the composite material 380 was based on the singular properties of each component as well 381 as on the synergetic properties that could be expected.

382 A linear response of the sensor array modified with PEDOT-PB-383 soluble coating towards DA oxidation, in the presence of AA, was 384 obtained over a concentration range from 10 to 50 μ M DA (see in-385 set of Fig. 5B). The corresponding linear equation was: i_{pa} (nA) = $0.46C_{DA}$ (μ M) + 30.6, with a correlation coefficient R^2 = 0.9925 386 387 (see inset of Fig. 5B), and a detection limit of 4.3 µM. The slopes 388 of the calibration graphs, i.e. the i_{pa} vs. DA concentration plots in 389 the absence and the presence of the interfering species, respec-390 tively, indicates that the presence of AA influences the DA oxida-391 tion. This is in agreement with data reported in the literature 392 concerning the simultaneous voltammetric determination of DA, 393 over a concentration range from 1 to $30 \,\mu\text{M}$, in the presence of 394 AA [29]

The electrocatalytic activity of PEDOT-PB-insoluble coating to-395 wards DA oxidation in the presence of AA was also investigated. 396 In this case there is no peak shaped anodic wave for the oxidation 397 398 of either analyte. Furthermore, the shape of the voltammograms is 399 similar to those recorded at unmodified microelectrode array, and 400 there is no improvement of the analytical performance. Hence the 401 PEDOT-PB-insoluble modified electrode is not suitable for analyt-402 ical applications.

4. Conclusions 403

404 Composite inorganic-organic coatings of various compositions 405 were prepared, i.e. containing both soluble ad insoluble form of

PB. The deposition procedures reported allow the preparation 406 in situ of both forms of PB as well as their electrochemical proper-407 ties in electrolyte solutions. The **PEDOT-PB-soluble** composite 408 material exhibited good electrochemical properties and electrocat-409 alytic activity towards dopamine oxidation. The **PEDOT-PB-insolu-**410 ble coating showed no further improvement of the analytical 411 performances with respect to the unmodified microelectrode ar-412 ray. The PEDOT organic coating as well as the **PEDOT-PB-soluble** 413 composite coating showed good stability in aqueous buffered solu-414 tion. The composite coating revealed to be porous enough to per-415 mit the free flux of potassium ions. The stability of the PEDOT-416 PB-soluble composite material results from the electrostatic inter-417 action between polarons in PEDOT and the negatively charge inor-418 ganic redox mediator. Low detection limit and linear responses 419 over wide ranges of analyte concentration in the presence of a 420 strong interferent have been obtained in the case of the PEDOT-421 PB-soluble coating. The good electrochemical and electrocatalytic 422 properties of this inorganic-organic composite material could be 423 exploited in the construction of new microelectrochemical sensors 424 as well as in similar analytical devices containing multiple sensing 425 elements, as in electronic tongues. 426

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