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Vincent Ball. Electrodeposition of coatings made from catecholamines, polyphenols and aminimalonitrile: Common features, perspectives and challenges. Progress in Organic Coatings, 2019, 131, pp.441-447. <10.1016/j.porgcoat.2019.02.027>. <hal-02933901>

HAL Id: hal-02933901

<https://hal.science/hal-02933901v1>

Submitted on 8 Sep 2020

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Electrodeposition of coatings made from catecholamines, polyphenols and aminomalonitrile: common features, perspectives and challenges

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Abstract: The possibility to functionalize almost all kinds of interfaces with catecholamines, catechols or aminomalonitrile to produce conformal films which can be subsequently functionalized with metal nanoparticles or organic molecules, revolutionized surface science in the last few years. However, when performed from solution using appropriate oxidants (in the case of catecholamines and catechols) or the appropriate pH range (in the case of aminomalonitrile), the film deposition is accompanied with precipitation of insoluble precipitates in solution implying a considerable loss of active molecules. This drawback can be circumvented on conductive substrates by performing deposition by cyclic voltammetry or by constant deposition methods. This short review aims to describe the state of the art in such deposition methods, to highlight common features of the obtained coatings and to give some perspectives to improve their properties, notably in terms of electronic conductivity.

Keywords: catechols, catecholamines, aminomalonitrile, electrochemical deposition.

1. Introduction

Versatile coating methods able to coat the surface of all classes of materials appear as a fascinating recent development in surface science. These coating methods relying on the oxidation of catecholamines [1], the adsorption of polyphenols [2-5] and a yet unknown

mechanism implying aminomalonitrile [6, 7] are bioinspired in essence. Indeed dopamine, the most representative catecholamine contains an ethyl amino group and a 1,2-benzenediol (also called a catechol) group able to mimic the functionality of L-Lysine and L-Dopa, respectively, in mussel adhesive proteins [8]. These amino acids are present in a high molar fraction in the mussel adhesion foot proteins (mefp) present at the byssus–water interface of mussels and allow for a strong underwater adhesion which is required for the mussel's survival. The use of polyphenols as versatile coating molecules is inspired from the formation of yellowish coatings on tea cups when put in contact with tea or reddish coatings on transparent glasses when put in contact with red wine. Finally, aminomalonitrile (AMN) is a molecule believed to have played an important role in prebiotic chemistry being a possible precursor of adenine [9-11]. However, the oxidation of catecholamines and of catechols as well as the polymerization of AMN occurs simultaneously on the surface of substrates immersed in the solution and in the solution itself. The latter oxidation/self-assembly or polymerization process leads to the formation of insoluble precipitates and hence to the loss of an important part of the initially provided monomers. On one hand, a lot of effort is now devoted to produce nanosized polydopamine (PDA), the final oxidation product of dopamine, by the addition of proteins or surfactants to the dopamine solution in the presence of an oxidant [12, 13]. On the other hand it has been shown that PDA can be deposited selectively on surfaces without oxidation of catecholamines in solution. It is the aim of this short review to summarize the obtained findings in this pretty new field of research. This review focuses on electrochemically triggered coatings based on catecholamines, catechols and AMN with the aim of comparing those coatings for future applications. Electrodeposition of paints is a traditional method to deposit coatings on solid conducting substrates [14]. A general review describing electrochemically triggered films based on macromolecules, including only a few

examples based on the molecules of interest therein, but providing general concepts is available [15].

2. Electrodeposition of Catecholamines

The electrodeposition of dopamine on gold electrodes has been shown to be highly dependent on the scan rate used during the cyclic voltammetry (CV) experiments in relation to the competition between the reversible oxidation/reduction of the catechol moiety with the intramolecular cyclisation (via a 1,4-Michael addition) to form leucodopaminochrome. When the CV experiments are performed at high potential scan rates, the characteristic time for the oxidation/reduction process is too short to allow for the intramolecular cyclisation to occur and no film deposition is observed [16]. However, at potential sweep rates lower than 50 mV.s^{-1} , in agreement with the determined rate constant for intramolecular cyclisation [17], the intramolecular Michael addition has time to occur before reduction of the quinone/semiquinone back to a catechol. In conditions of low scan rates, leucodopaminochrome and then 5,6-dihydroxyindole (DHI) are formed, as the first step of film deposition (Fig. 1). No film deposition through electrolymerization was observed below pH 4 owing to the protonated form of the ethylamino group on dopamine which hinders the intramolecular cyclisation.

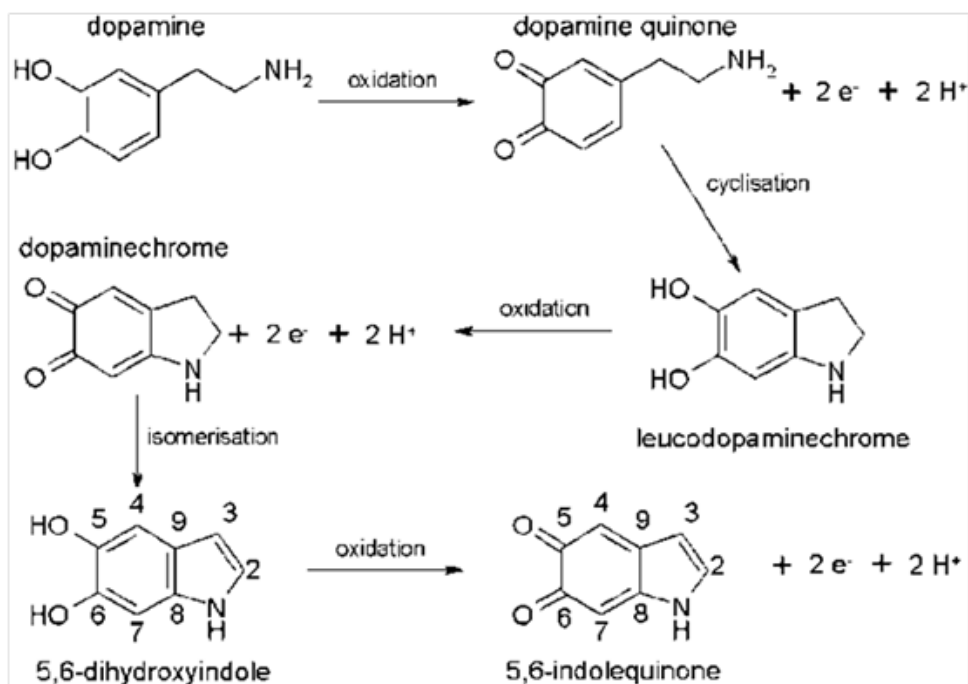


Fig. 1: Succession of electrochemical and chemical pathways leading from dopamine to 5,6-dihydroxyindole and 5,6-indolequinone, the building blocks of eumelanins and of polydopamine.

The peak position of the two oxidation peaks in the cyclic voltammetry curves were shifted cathodically by about 50 mV per pH unit, showing that the transfer of one electron is accompanied by the loss of one proton. The obtained electropolymerized dopamine based films were permselective towards cations. Later on, it has been shown that the permselectivity of PDA films, obtained through deposition from an aerated dopamine solution, can be switched from permselective for cations at high pH, where PDA carries a negative surface charge density to permselective for anions at pH below 5 where PDA is positively charged [18]. The change in zeta potential of PDA films, reflecting the sign of their surface charge have been measured by pH titration in a streaming potential device [19] and found consistent with the results published by Yu et al [18].

The permselectivity of PDA films depends also on the preparation method: films produced via cyclic voltammetry from a deoxygenated dopamine solution at pH 8.5 (in the presence of

150 mM NaNO_3) reach a critical thickness close to 45 nm (Fig. 2A, as measured from electrochemical quartz microbalance measurements) before becoming totally insulating and precluding further electron transfer from the solution to the working amorphous carbon electrode [20]. In these experiments, the potential sweep rate of the potential was 10 mV.s^{-1} as in [16]. The permeability of such films to ruthenium hexamine (a cationic redox probe) and to ferrocene methanol (a neutral redox probe) remains high up to almost the end of the film deposition whereas films obtained from solution deposition become impermeable to both redox probes after having reached about 10 nm in thickness. The same finding has been reported for the anionic hexacyanoferrate redox probe (Fig. 2B).

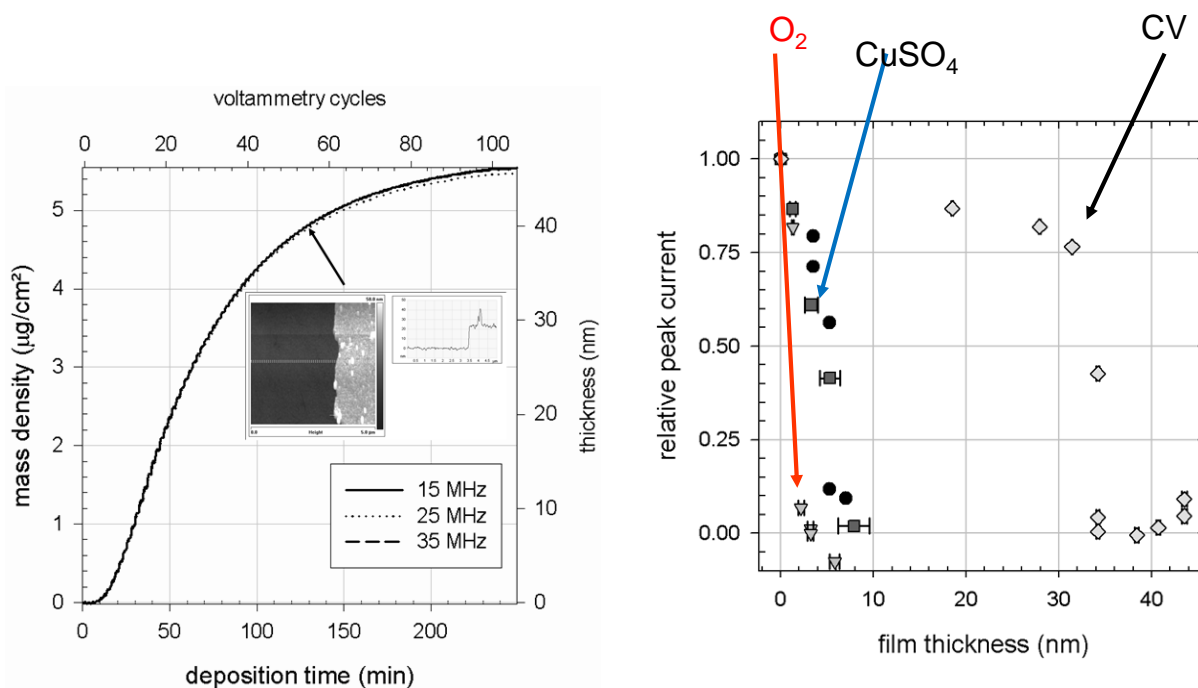


Fig. 2: Left part: thickness of a PDA film on a gold electrode during its deposition by means of cyclic voltammetry (CV) at a scan rate of 10 mV.s^{-1} in the presence of deoxygenated Tris buffer (50 mM at pH = 8.5) with 150 mM NaNO_3 . The dopamine concentration in solution was equal to 2 mg.mL^{-1} (10.6 mM). The frequency change of the quartz crystal on which the gold electrode was deposited was recorded in real time using a quartz crystal microbalance. The upper and lower horizontal axis represent the number of CV cycles and the deposition

time respectively. The inset represents the surface morphology, imaged by contact mode atomic force microscopy, of a film obtained after 50 CV cycles and needle scratching. The pristine gold electrode is on the left part and the PDA film on the right part of the surface topography.

Right part: Relative peak currents corresponding to the oxidation peak of potassium hexacyanoferrate (1 mM in 50 mM Tris buffer at pH = 8.5 + 150 mM NaNO₃) versus the PDA film thickness for films deposited from a dopamine solution either using O₂ or CuSO₄ as the oxidant or by electrodeposition through cyclic voltammetry. Modified from [20] with authorization.

Similar reports have reported the electrodeposition of conformal films on the electrode surface from dopamine containing solutions [21, 22]. Theoretical calculations based on the Density Functional Theory were used to corroborate the oxidation potentials at which dopamine is oxidized to dopaminequinone in a pH dependent manner [22].

In a somewhat different approach, PDA was deposited on carbon working electrodes for different time durations, and the electrochemical stability and permeability of the obtained coatings were characterized by means of cyclic voltammetry [23]. In addition the film thickness was determined in a consistent manner combining ellipsometry and Atomic Force Microscopy. Enzymes like Glucose Oxidase and Laccase could be successfully immobilized on the thin polydopamine films. The Laccase modified PDA films deposited on graphite electrodes showed an excellent sensibility, 152 mA.M⁻¹.cm⁻², for the detection of 2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt [23].

Electrodeposition of 5,6-dihydroxyindole (DHI) from Tris or phosphate buffer with pH values ranging from 7.0 to 7.8 were investigated under constant potential (CP, +0.5 V vs the

reference electrode) and by CV (from -0.4 to +0.4 V vs the reference electrode and at a potential sweep rate of 50 mV.s⁻¹). It was found that much thicker films, up to 400 nm thick, can be obtained by CP rather than by CV (250 nm) in the same overall time of 3000 s in the presence of Tris buffer. In the presence of phosphate buffer, the film thickness is decreased to 330 nm during CP deposition and increased to 300 nm by CV deposition respectively, the deposition lasting over 3000 s. In addition, it was found that the films deposited from Tris buffer adhered much better to the indium tin oxide electrodes than those obtained in phosphate buffer under similar deposition conditions [24]. This last finding is not unexpected owing to the presence of an amine group, still partly undeprotonated at pH 7.5 (The pK_a of Tris is 8.2) which can act as a nucleophile and bind to quinones on the oxidized DHI [25].

In terms of applications, PDA has been deposited via electrodeposition on the surface of cardiovascular stents (1 mg.mL⁻¹ dopamine in the presence of 25 mM Tris buffer at pH = 7.4 +140 mM NaCl + 3 mM KCl under permanent N₂ bubbling to remove dissolved O₂, potential sweep rate: 20 mV.s⁻¹). These PDA coated stents allowed grafting of vascular endothelial growth factor improving the adhesion of endothelial cells with respect to uncoated stents [26]. From a physicochemical point of view it was found that the coatings obtained through cyclic voltammetry of dopamine solutions at pH = 7.4 grew faster than polydopamine films deposited in an oxygenated Tris buffer at pH = 8.5 [26].

3. Electrodeposition of catechols.

Pyrocatechol (the structure of which is displayed in the inset of Fig. 3) is the most simple catechol molecule and is known to be easily oxidizable and to be able to act as a ligand for metal cations like Fe³⁺, Cu²⁺, etc...In addition its structure is much simpler than that of dopamine, lacking the ethylamino group. Hence, no competition with an intramolecular addition process can occur during its oxidation. For these reasons, pyrocatechol constitutes an ideal molecule to investigate the electrodeposition of catechols on electrodes. When a

pyrocatechol solution at pH 5.0 or 7.0 is subjected to cyclic voltammetry at potential sweep rates between 5 and 100 mV.s^{-1} , a progressive decrease of the oxidation-reduction current is observed and the process appears irreversible when the number of performed CV cycles increases (Fig. 3).

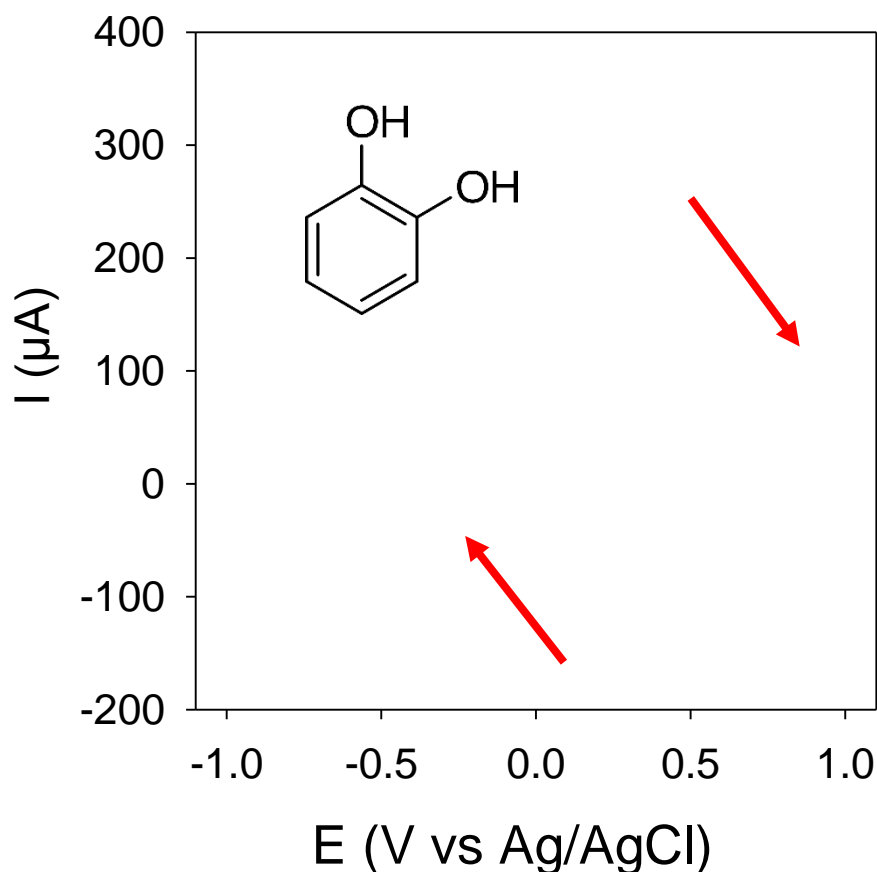


Fig. 3: Cyclic voltammetry of a pyrocatechol solution (2 mg.mL^{-1} in the presence of 50 mM sodium acetate buffer at pH = 5.0) on an amorphous carbon electrode at a scan rate of 50 mV.s^{-1} . The red arrows show the influence of the number of potential sweep cycles and the structure of pyrocatechol is displayed as an inset. Modified from [27] with authorization.

The pyrocatechol based coating obtained on the electrode surface is by itself electroactive with a saturation of the capacitive current (obtained in the absence of any external probe)

reached for films obtained after 10 CV cycles (Fig. 4A). In the same time, the films deposited from pyrocatechol solutions become progressively impermeable to a redox probe like hexacyanoferrate (Fig. 4B). The film permeability for the redox probe decreases when the scan rate used during the CV experiments decreases [27]. Interestingly, at pH = 5.0, the electrodeposition of pyrocatechol is much more efficient than that of dopamine (Fig. 4B). This is easily understandable on the basis of the presence of a protonated ethylamino group on dopamine at such a low pH value. This protonated amine hinders the intramolecular addition on the oxidized dopaminequinone and the subsequent formation of leucodopaminechrome (see Fig. 1). Indeed at pH 8.5, in deoxygenated solutions, the electrodeposition of dopamine is very efficient leading to the formation of a film impermeable to hexacyanoferrate after only 30-40 CV cycles (Fig. 2). At pH 5.0, under the same experimental conditions of potential scan, the permeability for hexacyanoferrate is only reduced by 40 % after 50 cycles (Fig. 4B)

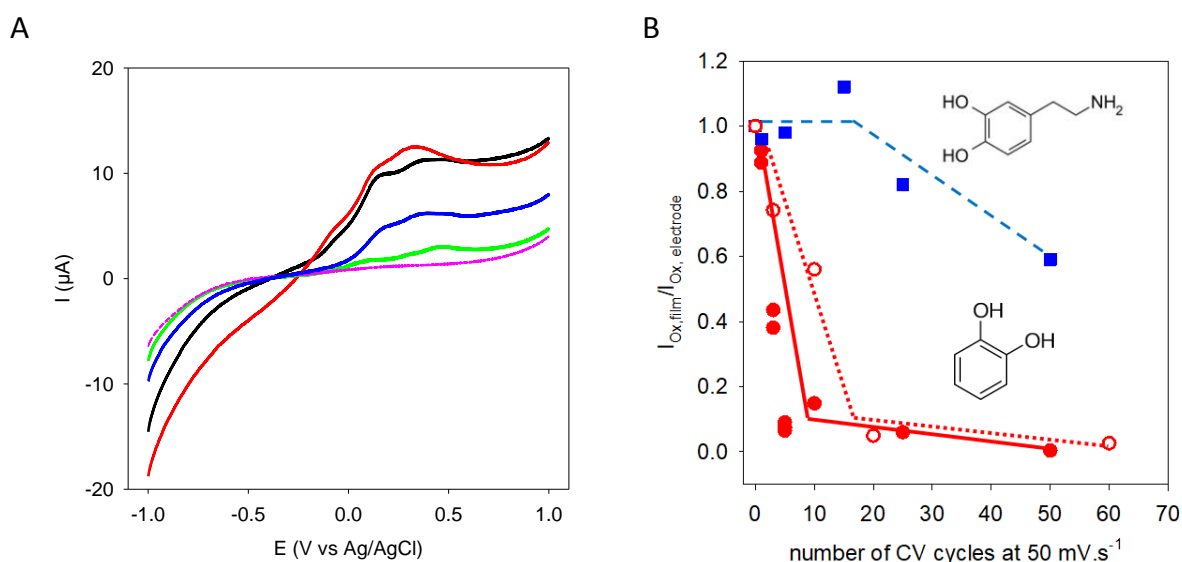


Fig. 4: A: Capacitive curves (only the anodic branch is represented) acquired in the presence of 50 mM sodium acetate buffer at pH 5 and 100 mV.s⁻¹ after a different number of CV cycles performed at 50 mV.s⁻¹ in the presence of pyrocatechol at 2 mg.mL⁻¹ : — 1 cycle,

— 5 cycles, — 10 cycles, and — 50 cycles. — corresponds to an experiment in which the electrode was incubated in a 2 mg.mL⁻¹ pyrocatechol solution during 1h but without potential scanning before acquisition of the capacitive curve (100 mV.s⁻¹) in the presence of 50 mM sodium acetate buffer at pH=5.0.

B: : Evolution of the relative oxidation current of the hexacyanoferrate anions as a function of the number of CV scans performed at pH 5.0 in the presence of pyrocatechol (—●—) or dopamine (---■---) . Pyrocatechol and dopamine were dissolved at 2 mg.mL⁻¹ and their oxidation was performed by CV at a scan rate of 50 mV.s⁻¹. Some additional experiments were performed at the same concentration in pyrocatechol but at scan rates of 100 mV.s⁻¹ (····○····). The lines are aimed to guide the eye. Modified from [27] with authorization.

When tannic acid (TA, the structure is displayed in the inset of Fig. 5A) is mixed with a solution containing Fe²⁺ cations with a typical ratio of 2.5 cations per polyphenol, a constant increase in the film thickness is obtained by applying a constant current density (typically 6. 25 $\mu\text{A.cm}^{-2}$) in a potential window allowing for the oxidation of Fe²⁺ into Fe³⁺ but only minor oxidation of TA (which occurs at higher potentials) at pH = 3.0. [28] (Fig. 5A). The film thickness is proportional to the deposition time up to 70 min of deposition at a current density of 6.25 $\mu\text{A.cm}^{-2}$ (Fig. 5A) but saturation in film deposition is obtained for shorter deposition times when the deposition is performed at higher current densities. The film deposition rate can be increased by increasing the Fe²⁺/TA ratio in the reaction mixture up to a plateau value of 10 (Fig. 5B). Characterization of the films by X-ray photoelectron spectroscopy showed that the obtained films contain a majority of Fe³⁺ cations over Fe²⁺ cations and that the TA/iron content of the films is close to 2 which is compatible with the

formation of iron –biscatechol complexes. Similar electrodeposited films can be obtained by using other polyphenols like gallic acid or rosmarinic acid [28].

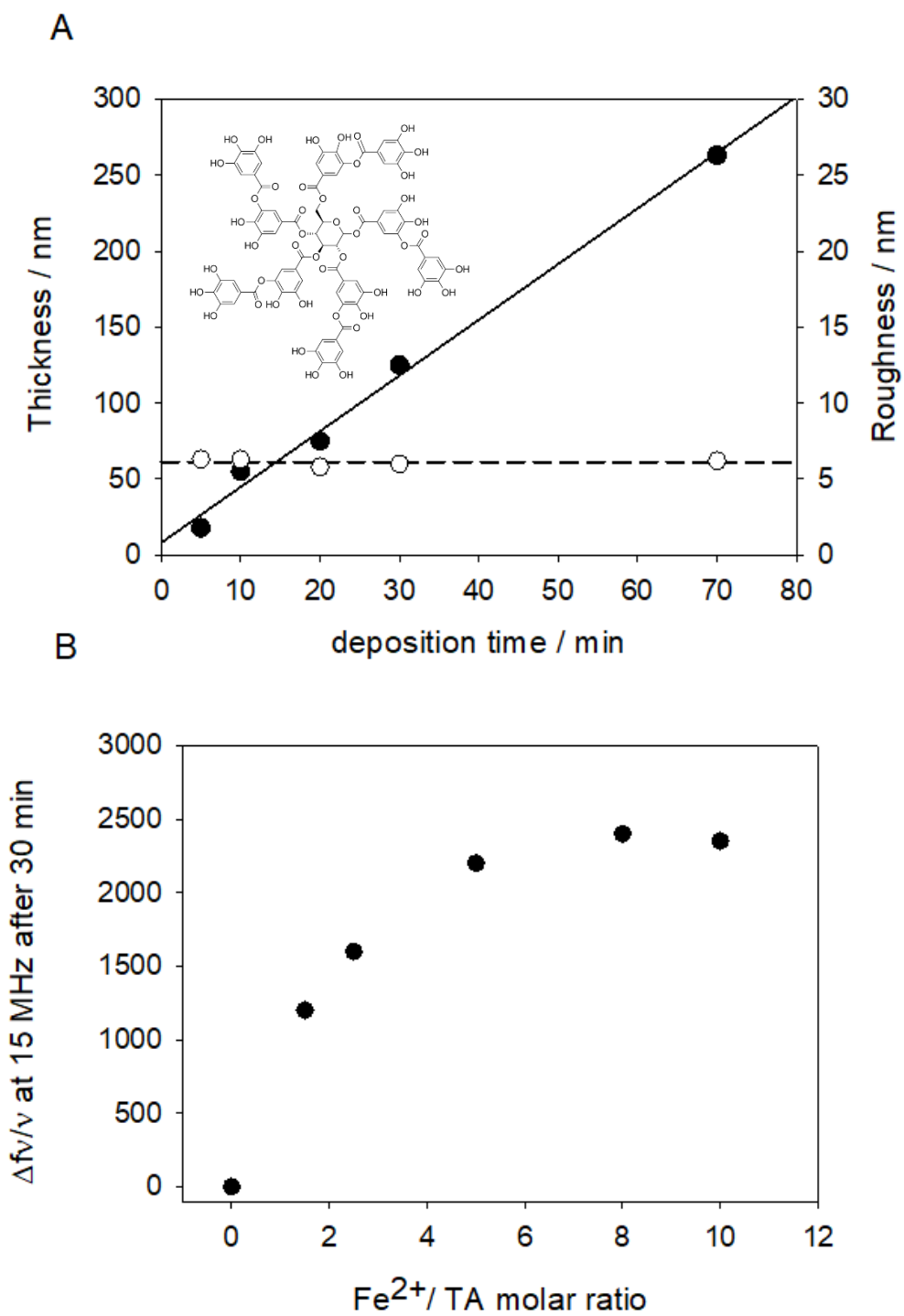


Fig. 5: A: thickness of coatings obtained through electrodeposition of a tannic acid /iron nitrate mixture ($\text{Fe}^{2+}/\text{TA} = 2.5$ at $\text{pH} = 3.0$) as a function of the deposition time under a constant current density of $6.25 \mu\text{A}.\text{cm}^{-2}$. The film thickness was obtained with Atomic Force Microscopy after needle scratching of the deposit to measure the profile height change between the uncoated ITO substrate and the top of the film. The structure of tannic acid (TA) is shown as an inset.

B: Change of the reduced frequency of the ITO coated quartz crystal, $\Delta f_v/\nu$, after 30 min of electrodeposition at $\text{pH} = 3.0$ and a current density of $6.25 \mu\text{A}.\text{cm}^{-2}$ as a function of the Fe^{2+}/TA ratio in solution. Modified from [28] with authorization.

4. Electrodeposition of aminomalonitrile

Aminomalonitrile (its structure is displayed in the inset of Fig. 6A in the form of a paratoluene-sulfonate salt) dissolved in basic phosphate buffer solutions allow to coat all kinds of materials with a conformal coating [6, 7]. It was recently found that performing CV scans at variable sweep rates from AMN solutions at $\text{pH} 6.0$ allowed for the deposition of AMN films (Fig. 6A) having the same composition as those obtained from solution deposition but at $\text{pH} 8.6$, as inferred from XPS spectroscopy. It has to be noted that no deposition occurs from AMN solutions at $\text{pH} 6.0$ in the absence of applied potential ramps [29]. Those films are impermeable to redox probes like potassium hexacyanoferrate (Fig. 6B). At the present stage, the reaction mechanism leading to films from AMN containing solutions under the application of CV scans is not yet known.

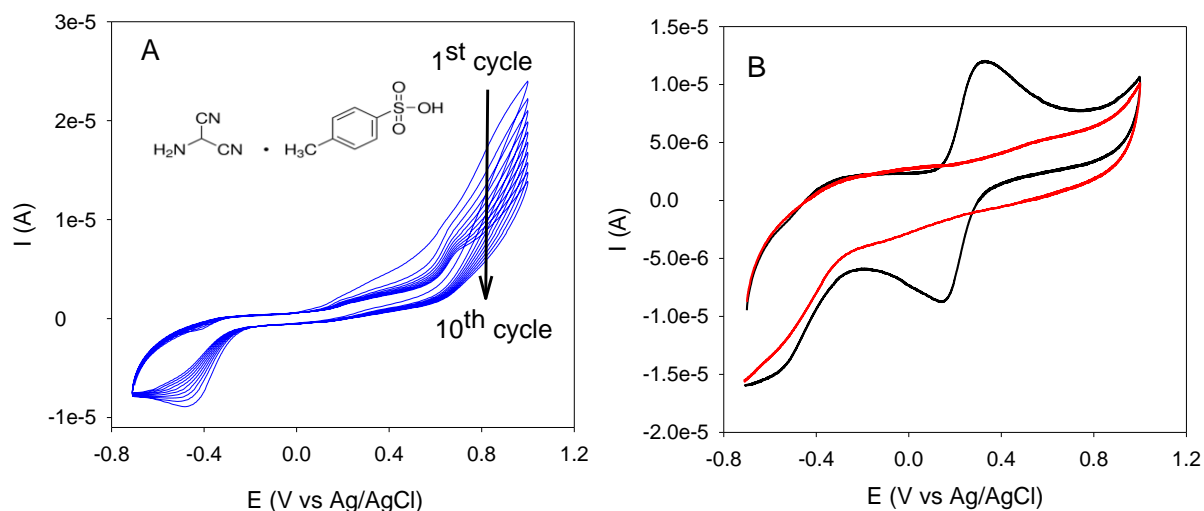


Fig. 6: A: Superposition of 10 successive CV cycles (performed at 50 mV.s^{-1}) in the presence of AMN at 10 mg.mL^{-1} (—). The black vertical arrow indicates the evolution of the faradaic current from the first to the 10th CV cycle. The structure on aminomalonitrile paratoluene-sulfonate salt is also shown.

B: Cyclic voltammogram of a potassium hexacyanoferrate solution (1 mM in the presence of 50 mM sodium phosphate buffer) performed at 100 mV.s^{-1} on a pristine amorphous carbon electrode (—) and on the same electrode after 10 potential sweep cycles in the presence of 10 mg.mL^{-1} AMN (—). The electrochemical deposition of the AMN based film was performed at a potential scan rate of 50 mV.s^{-1} in the presence of sodium phosphate buffer at $\text{pH} = 6.0$.

Modified from [29] with authorization.

5. Comparison between the electrodeposition of catecholamines, catechols and AMN

All the films obtained by electrodeposition of catecholamines, catechols or AMN display as common features an excellent adhesion to the electrode surface but a poor electrical

conductivity. This last property is immediately observable upon performing the CV scans: the oxidation current decreases progressively from one scan to the next one (see Fig. 3 and 6). In addition, electrochemical impedance spectroscopy experiments on all those films have shown an increase in the impedance of the films with their thickness (Fig. 7). In the case of films prepared from a small number of CV scans, the impedance spectra could be fitted with the Randless equivalent circuit [30]. The obtained data highlight a clear increase in the resistance to the electron transfer as well as an increase in the Warburg impedance, characterizing the diffusion of electroactive species from the solution to the electrode through the deposited film [30] (Table 1).

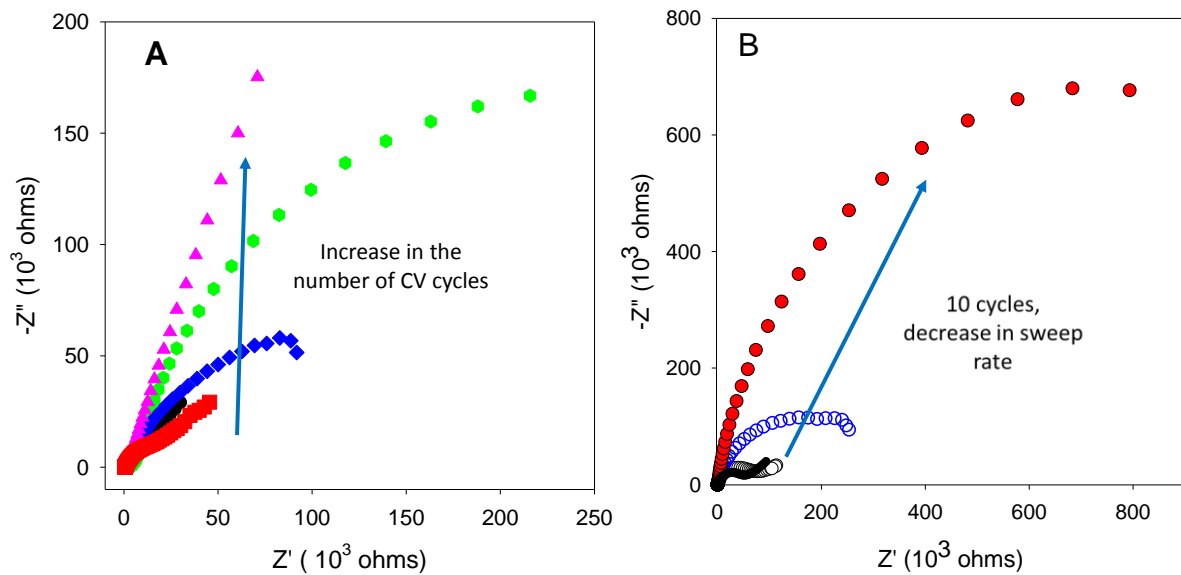


Fig. 7: Examples of electrochemical impedance spectra of electrodeposited pyrocatechol (panel A) and AMN based (panel B) films.

A: (■) $n=3$, (◆) $n= 10$, (●) $n = 20$, (▲) $n = 60$ CV cycles performed at $v = 20 \text{ mV.s}^{-1}$.

B: films obtained after 10 CV cycles at (●) 100 mV.s^{-1} , (○) 50 mV.s^{-1} , (○) 20 mV.s^{-1} , (○) 10 mV.s^{-1} .

Modified from [27] and [29] with authorization.

Monomer and reference	Experimental conditions	R_1 ($\Omega \cdot \text{cm}^{-2}$)	R_2 ($\Omega \cdot \text{cm}^{-2}$)	CPE^n ($\mu\text{F} \cdot \text{cm}^{-2}$)	n	W (Ω)
Dopamine [20]	30 cycles, 10 $\text{mV} \cdot \text{s}^{-1}$, deoxygenated Tris buffer, pH = 8.5	97 ± 7	$(4.92 \pm 0.23) \times 10^3$	3.40 ± 0.20	0.825 ± 0.008	$(5.04 \pm 0.15) \times 10^3$
Dopamine [20]	40 cycles, 10 $\text{mV} \cdot \text{s}^{-1}$, deoxygenated Tris buffer, pH = 8.5	131 ± 4	$(1.23 \pm 0.03) \times 10^4$	3.50 ± 0.10	0.828 ± 0.004	$(1.12 \pm 0.03) \times 10^4$
Dopamine [20]	50 cycles, 10 $\text{mV} \cdot \text{s}^{-1}$, deoxygenated Tris buffer, pH = 8.5	127 ± 6	$(3.72 \pm 0.63) \times 10^4$	2.00 ± 0.05	0.851 ± 0.004	$(1.25 \pm 0.07) \times 10^4$
Dopamine [20]	70 cycles, 10 $\text{mV} \cdot \text{s}^{-1}$, deoxygenated Tris buffer, pH = 8.5	97 ± 5	$(6.13 \pm 0.14) \times 10^4$	2.20 ± 0.05	0.853 ± 0.04	$(1.03 \pm 0.12) \times 10^4$
AMN [29]	10 cycles, 100 $\text{mV} \cdot \text{s}^{-1}$,	202 ± 15	$(5.05 \pm 0.26) \times 10^4$	3.24 ± 0.08	0.85 ± 0.01	$(1.06 \pm 0.1) \times 10^4$

	phosphate buffer, pH = 6.0		10^4			
AMN [29]	10 cycles, 50 mV.s^{-1} , phosphate buffer, pH = 6.0	203 ± 17	$(7.66 \pm 0.29) \times 10^4$	26.6 ± 0.9	0.86 ± 0.01	$(1.04 \pm 0.20) \times 10^4$
AMN [29]	10 cycles, 50 mV.s^{-1} , phosphate buffer, pH = 6.0	227 ± 27	$(3.09 \pm 0.32) \times 10^5$	81.2 ± 3.0	0.83 ± 0.02	$(2.5 \pm 0.7) \times 10^5$

Table 1. Results obtained by fitting the Randless equivalent circuit to electrodeposited films from either dopamine or AMN solutions. The experimental conditions are indicated in the second column.

An elegant way to increase the conductivity of PDA based films was to co-deposit dopamine and pyrrole by chronoamperometry at constant potential of 0.5 V versus the saturated calomel electrode and in the presence of sodium phosphate buffer at pH = 6. The conductivity of the obtained films was characterized by means of a four-point probe and was found maximal at a dopamine/pyrrole molar ratio of 0.2 in the feed solution [31] (Fig. 8). As an additional advantage of performing the electrodeposition from a dopamine-pyrrole mixture, with respect to pyrrole alone, was to improve the adhesion of the conductive film to the electrode surface. By improved adhesion, it is meant that the composite film does not spontaneously delaminate from the electrode which was the case for the electrodeposited

polypyrrole film. This property is due to the strong adhesion ability of catechol moieties to almost all known materials [1, 2].

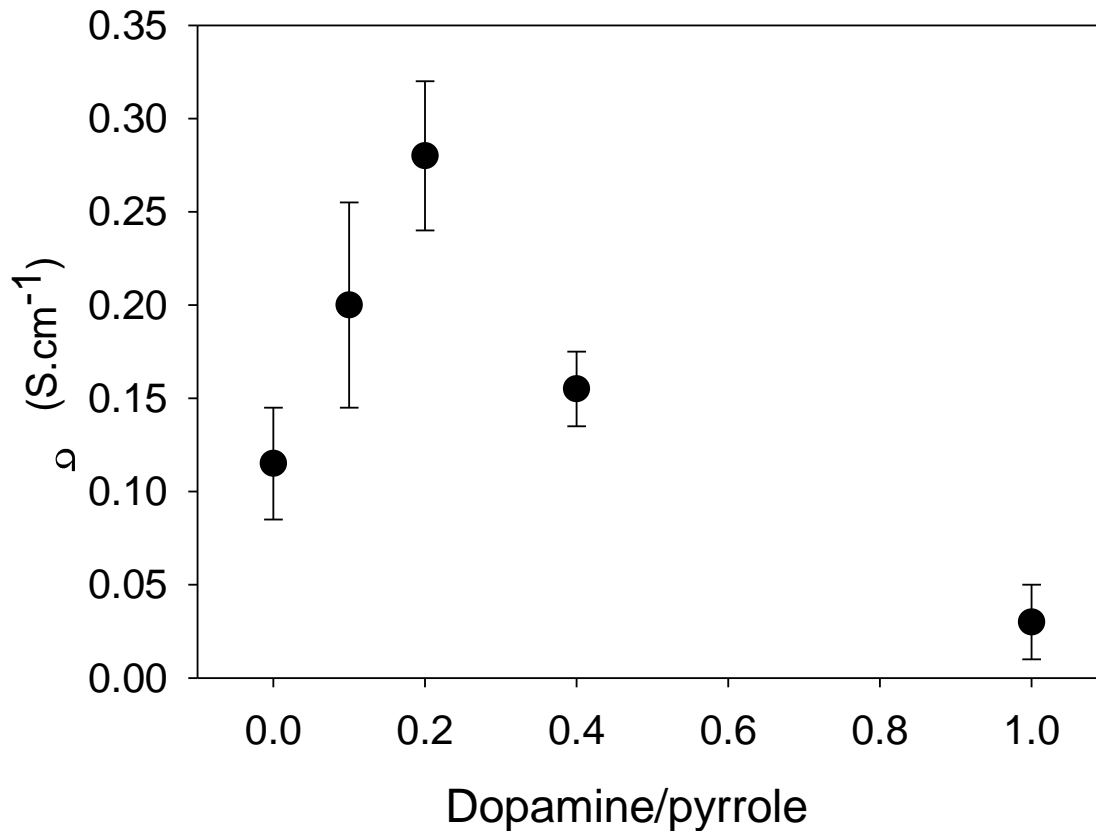


Fig. 8: Evolution of the conductivity of PDA/polypyrrole films as a function of the dopamine/pyrrole ratio in the feed solution. The error bars correspond to one standard deviation obtained over $n = 3$ experiments. Modified from [31] with authorization.

6. Conclusions and perspectives

In recent years it has been shown the CV and CP methods can be used to deposit catecholamine, catechols or AMN based films on solid surfaces without losing soluble monomers as in the case where deposition is performed in the presence of suitable oxidants (in the case of catecholamines and catechols) or at the appropriate pH (in the case of AMN). This coatings can all be produced in a one step process and are conformal and biocompatible.

However their major drawback is their lack of electrical conductivity which not only limits their growth process to a limited thickness (after which no electron transfer between the monomer containing solution and the working electrode is possible) but also limits their applications. The electrodeposition of such coatings based on catecholamines, catechols and AMN in the presence of carbon nanotubes, in analogy with aniline or pyrrole based composite coatings [32, 33], should allow to open new avenues in the design of conductive and biocompatible coatings for applications in biomaterials science. In particular, such coatings could constitute excellent interface for the electrostimulation of neurons. Additionally, those kinds of coatings should be evaluated for their anticorrosion properties. Their impermeability to ions and their excellent stability on the deposited substrates as well as their inherent antioxidant properties make them excellent candidates for such applications.

Finally, additional research efforts are also required to understand the reaction pathways leading to films through the application of CV scans in the presence of catechol and AMN containing solutions.

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