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Deposition Mechanism and Properties of Thin Polydopamine Films for High Added Value Applications in Surface Science at the Nanoscale

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Abstract Polydopamine films have been introduced by Messersmith et al. as a possible “versatile” surface functionalization method allowing to coat the surface of almost all known materials even superhydrophobic surfaces. These new kinds of coatings also confer a plethora of functionalities to the coated materials owing to the complex chemistry of the catechol quinone moieties present on the surface of polydopamine. These coatings may hence become an interesting alternative to established surface coatings like self-assembled monolayers and polyelectrolyte multilayered films. In this review, we describe the knowledge acquired in the last 3 years about the deposition mechanisms of polydopamine films, their properties, and various applications in surface science at the nanoscale.

Keywords Surface functionalization · Polydopamine · Melanin · Reaction mechanisms · Biocompatible films

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1 Introduction

In modern technology, there is an urgent need to improve the coating of the surfaces of materials to achieve better film homogeneity and stability and enhanced functionality and versatility of the deposition method. Material coatings are aimed not only to protect the underlying materials from external agents such as strong oxidants but also to confer them with new functionalities. Indeed, the first interaction a material establishes with its environment is through its surface, and a stable and tight monolayer of molecules is sufficient to completely change the surface chemistry of a material. This is exemplified by the value of its surface tension [1]. Biomaterials are a marvelous example of this rule; when put in a living organism, their fate depends on their biocompatibility (no release of toxic ions or molecules) and the nature of the first molecules that interact with their surface. These “first adsorbing” molecules are most often proteins [2]. In case where these proteins present strong interactions with the cells from the host organism, one can expect a safe recolonization of living tissue around the implanted material. On the other hand, when some bacteria remain adherent on the surface of the implanted biomaterial, an inflammatory cascade may lead to the rejection of the implant with a lot of complications for the patient [3].

More generally, self-assembled structures from living organisms offer wonderful examples of optimized materials with respect to adhesion [4] or mechanical properties [5, 6] and for the design of functionalized surfaces. Among the most fascinating biomaterials owing to their hierarchical structure, one can distinguish nacre [7], biosilica [8], silk [9–11], and melanin. Melanin is the natural photoprotectant of the human skin and plays a major role in many pathological processes. Natural melanin, either the black eumelanin or the

reddish-brown pheomelanin, is obtained through enzymatically catalyzed processes. The enzyme tyrosinase present in the melanosomes of the skin catalyzes the hydroxylation of tyrosine to produce 3,4 dihydroxy-L-phenylalanine. The synthetic pathways used by cells to produce the melanin pigments are called melanogenesis, the current understanding of which is by far not complete and has been reviewed recently [12]. The reader interested in melanogenesis may find several specialized books [13] and reviews [14, 15].

The most fascinating features of melanin lie in its electronic and optical properties. It was assumed to behave like an amorphous semi-conductor [16], and its direct current conductivity values are reported to fluctuate between 10^{-5} and 10^{-13} S cm⁻¹. There is increasingly strong evidence that such a large range of conductivity values, which are temperature dependent, are related to hydration effects. To clarify this point, the adsorption isotherm of water on melanin has only been investigated very recently. Water adsorbs on melanin grains owing to the hydrophilicity of the chemical groups present at its surface [17]. From the point of view of the optical properties, the most salient features of melanins are the broadband and monotonous absorption spectrum (with very small contribution from light scattering [18, 19]), the very weak emission quantum yield [20], and the violation of the mirror rule between the absorption and emission spectra [14].

The aim of the present article is to review the most recent advances in melanin and melanin-inspired materials used for applications as biologically inspired surface coatings. The interest in using catechol amine-derived materials in surface chemistry comes from the important fraction (up to 40 mol%) of 3,4 dihydroxyphenyl-L-aniline in the amino acid sequence of the *Mytilus edulis* foot protein (MEFP)5 which allows for the strong adhesion of mussels to solid surfaces in the presence of high shear stresses [21].

2 The Need for a Universal Surface Functionalization Method

Since ancient times, the coating of the material surfaces has been a major concern not only for esthetic reasons but also to improve the stability and the longevity of materials. Protection against corrosion is emblematic for the need to coat metallic surfaces with films impermeable to corrosive agents. Painting has been and still is a major coating technology and can afford robust coatings provided good adhesion between the material and the painting is attained. However, the need for thin films of controllable thickness and adjustable functionality appeared during the twentieth century. Among these technologies allowing to reach such requirements, one can cite electropolymerization [22], the deposition of Langmuir–Blodgett films [23, 24], self-

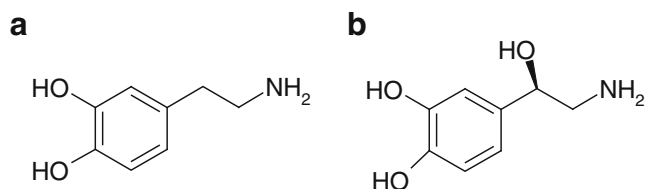
assembled monolayers [25], the deposition of films in a layer-by-layer fashion [26–28], and plasma deposition [29].

All these methods have specific advantages and drawbacks but share a certain surface specificity. For instance, self-assembled monolayers can only be deposited on the surface of noble metals (Pt, Ag, Au) using molecules carrying thiol groups or on the surface of oxides using alkylsilanes. Layer-by-layer deposition of polyelectrolyte multilayer (PEM) films requires the use of charged surfaces: The deposition of PEMs on poly(tetrafluoroethylene) is possible only after priming with a plasma deposited allylamine [30], whereas chemical (physical or vapor) deposition techniques work under vacuum.

From this perspective, there is a clear need to develop universal coating technologies allowing to functionalize the surface of almost, if not all, classes of materials at the material's surface solvent interface. The types of glues used by living organisms can be a marvelous source of inspiration to develop such universal coatings. Mussels are a particularly well-suited example: They adhere strongly to wood or stones in conditions of high shear stresses, the rate of water flow being as high as 10 ms⁻¹. The adhesion of these organisms to solid surfaces is possible through specific proteins called *M. edulis* foot proteins at the end of the mussel's byssus [31]. A close look at the amino acid sequence of such proteins shows that they are enriched, up to 40% in molar fraction, in 3,4-dihydroxy-L-phenylalanine, a hydroxylated version of the natural amino acid tyrosine [32]. Polymers carrying catechol groups allow for impressive bond strength with surfaces and allow to mimic the bond strength afforded by MEFP5 [33].

These findings have allowed the development of new surface functionalization methods based on molecules carrying catechol groups. These methods have been recently reviewed elsewhere [34].

In this review, we will mainly focus on films made through oxidation processes in the presence of catechol amine solutions (as dopamine or norepinephrine, whose structure is depicted in Scheme 1). The feasibility and the universality of such coatings with respect to the nature of the substrate to be coated has been demonstrated by Lee et al. [35, 36].



Scheme 1 Chemical formula of dopamine (a) and norepinephrine (b), the two most common catechol amines used to produce polydopamine films on solid surfaces

As we will see in the next paragraph, polydopamine coatings produced through an oxidation process allow us to control the deposition rate of the films. There are, however, other methods that allow one to produce coatings with similar properties using natural or synthetic melanin particles. Among such methods, one can cite spray coating [37], spin coating [38], solvent casting [39], or electrochemical deposition from basic melanin suspensions [40]. In general, however, solid-state melanin is a hard to process material owing to its insolubility in most organic solvents. Fortunately, it is soluble in strongly alkaline aqueous solutions. This makes melanin a material hard to characterize and to understand, which is mandatory owing to its fascinating properties [13, 14]. The possibility to produce melanin-like coatings on many different substrates is not only a formidable opportunity in surface science but also an ideal platform to characterize the properties of the material since many analytical techniques like X-ray photoelectron spectroscopy, atomic force microscopy, etc. are well suited for the analysis of planar surfaces.

3 Mechanism of Polydopamine Film Formation

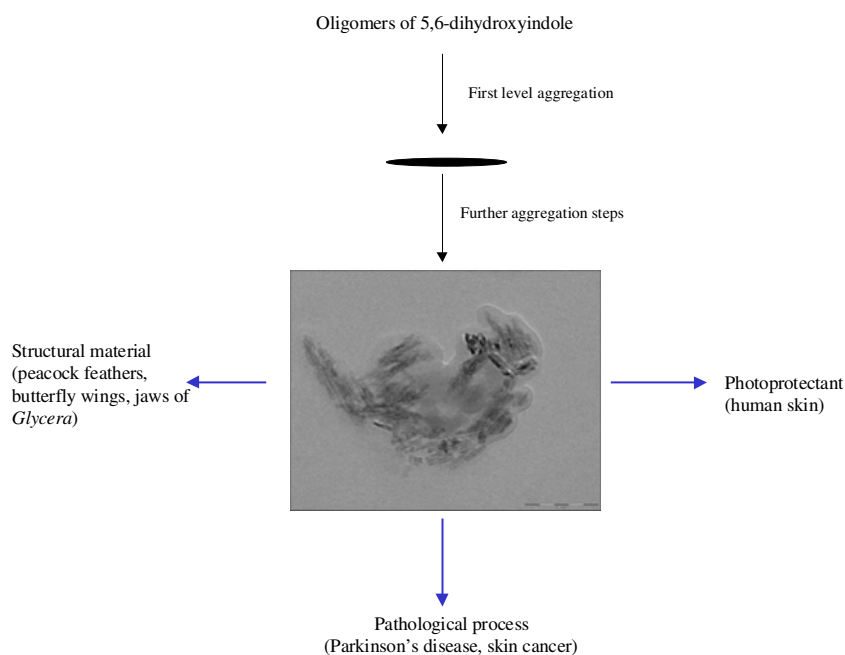
Eumelanins are fascinating materials owing to their bio-optoelectronic properties but also challenging owing to their structural complexity [41]. A recent and complete review of the physicochemical properties of eumelanin includes their optical, electrical, and mechanical properties [42]. The basic knowledge and the known properties of melanin, in solution, are summarized in Fig. 1.

The most important aspects with respect to polydopamine films are their optical and electrical properties. Of even more

fundamental importance is the question of polydopamine's structure: Is it a polymer or a hierarchical supramolecular and amorphous aggregate? In case where polydopamine is a polymer (the name spontaneously implies a polymeric nature, but to our knowledge no experimental proof is available at present), this would perfectly justify the employed denomination for the films produced during oxidation of dopamine solutions in the presence of the substrate to be coated. There is, however, strong evidence that polydopamine is a eumelanin-like material for which the most probable model is that of a hierarchical aggregate of oligomers (the so-called stacked protomolecule model) made from 5,6-dihydroxyindole (Fig. 1). This model relies mostly on investigations performed using scanning tunneling microscopy [43]. Recent calculations performed at the density functional theory level suggest that the most stable aggregate of 5,6-dihydroxyindole is a tetramer having the planar geometry of a phtalocyanine (Fig. 2) [44].

The “stacked protomolecule model” allows us also to explain the X-ray diffraction studies performed by Thathachari and Blois [45] as well as the atomic force microscopy data of Clancy and Simon [46] and the matrix-assisted laser desorption mass spectra data of Pezzella et al. [47]. Unfortunately, in the case of polydopamine films produced according to the method proposed by Lee et al. [35], there is not yet a definitive proof that the obtained coatings display the characteristic features of eumelanin. In the case where the used catecholamine was norepinephrine, the authors called the obtained coating “polynorepinephrine” [36]. Since there is no proof that these coatings are different from those made from dopamine, we call all the coatings obtained from catecholamines in the presence of oxidants, polydopamine coatings in a systematic manner. There is now accumulating evidence that the polydopamine

Fig. 1 Multistep self-assembly of oligomers made from 5, 6-dihydroxyindole to yield a hierarchical and multifunctional material, melanin. The scale in the TEM micrograph corresponds to 100 nm; personal data of V. Ball



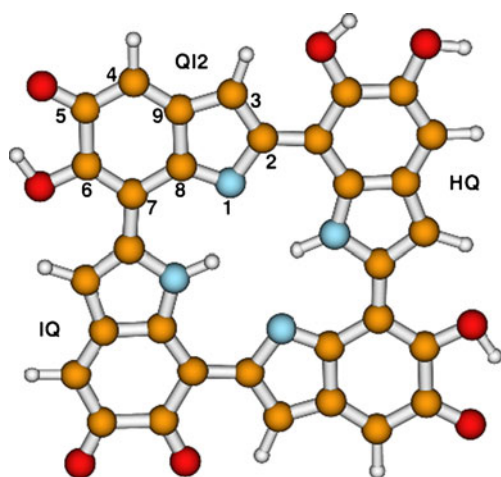


Fig. 2 Structural model of the most stable tetramer of 5,6-dihydroxyindole. Reproduced with permission from [44]

coatings share a lot of common features with eumelanin, namely:

- Their composition, based on X-ray photoelectron spectroscopy, is similar to that of eumelanin [48].
- The solution from which these coatings are made containing grains whose solid-state NMR spectrum is very similar to that of eumelanin [48].
- The surface morphology (Fig. 3) of the obtained coatings is made from platelets a few hundred nanometers in diameter, very similar to that found for the eumelanin grains found in natural organisms like in the *Glycera* jaws [49].

- The UV–vis [48] (Fig. 4) and infrared spectra of the coatings are similar but not identical to those of synthetic eumelanin [50].

The influence of the used oxidant has also been investigated: It appears that oxidants other than oxygen are efficient in the deposition of polydopamine films. It has been shown that dopamine solutions containing ammonium persulfate, sodium periodate, and sodium perchlorate allow for the deposition of films having the composition of polydopamine [51]. Of the highest interest is that the deposition of polydopamine occurs at a pH of about 4 when ammonium persulfate is the oxidant. The same finding holds true when copper (II) sulfate is the oxidant [52]. These findings show that some fundamental investigations about the oxidation mechanism of dopamine into dopamine quinone, which is known to be a pH-dependent equilibrium, are necessary (Scheme 2).

This equilibrium is shifted to the reactant when the pH decreases, and hence, the deposition of polydopamine should not occur in acidic conditions. This is indeed the case when the dopamine solutions are aerated: The deposition rate of the film vanishes to zero when the pH is below 5.5 (V. Ball et al., to be submitted for publication). However, in the presence of persulfate anions or Cu^{2+} cations, the deposition occurs even at pH 4. More interesting is that the deposition of the coating occurs up to thicknesses higher than the critical value of 45 nm obtained when O_2 is the oxidant (Fig. 5a) [52].

The films produced through oxidation in the presence of Cu^{2+} contain 2% (in molar fraction) of Cu^{2+} cations and not

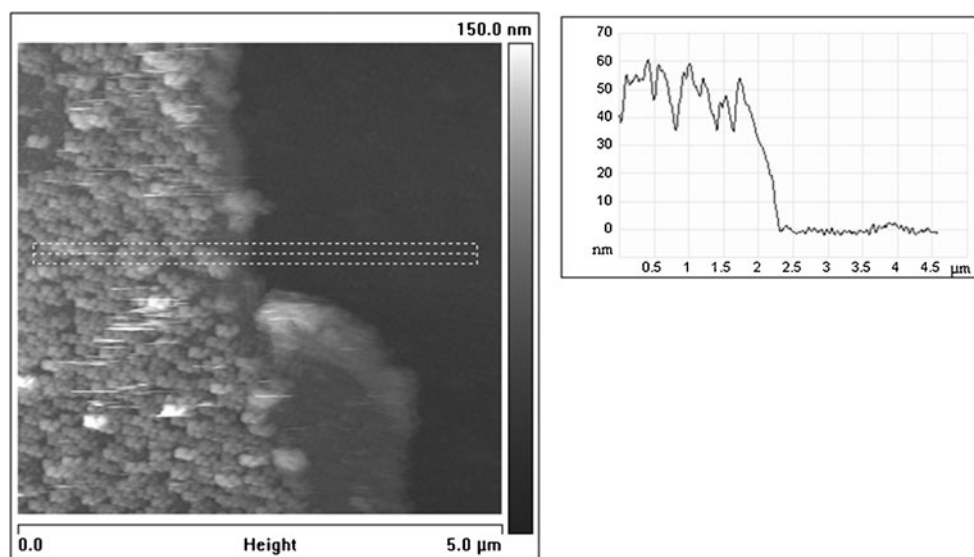


Fig. 3 Surface topography of polydopamine films obtained by exposing silicon substrates to a dopamine solution (2 mg mL^{-1} in 50 mM Tris buffer at pH 8.5) during 24 h. The surface topography has been obtained in the dry state by atomic force microscopy operated in the contact mode. The polydopamine film has been needle-scratched to

allow for film thickness measurement. The *right part* of the image corresponds to the naked silicon substrate. The *right panel* represents the average surface profile in the region corresponding to the hatched rectangle of the *left image*. Adapted from [80] with permission from Elsevier

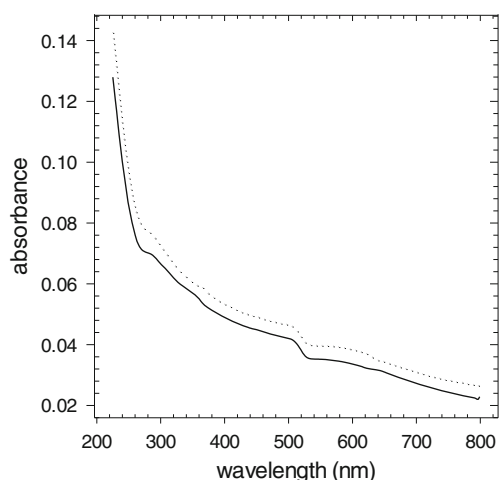


Fig. 4 UV-vis spectra (two independent experiments) of polydopamine films produced by exposure of a quartz slide to eight freshly prepared dopamine solutions (2 mg mL^{-1} in the presence of 50 mM Tris buffer at $\text{pH } 8.5$). Each exposure lasted over 5 min without rinse with buffer solutions between two deposition steps. From [48] with authorization from the American Chemical Society

metallic copper as expected (indeed copper is obtained through reduction of Cu^{2+}). The incorporation of Cu^{2+} in the film may well be related to the well-known affinity of melanin to metallic cations [53–55]. The very peculiar growth rate of the film's thickness may well be related to the presence of Cu^{2+} cations in solution which could play the role of a glue allowing the agglomeration of small oligomers of polydopamine.

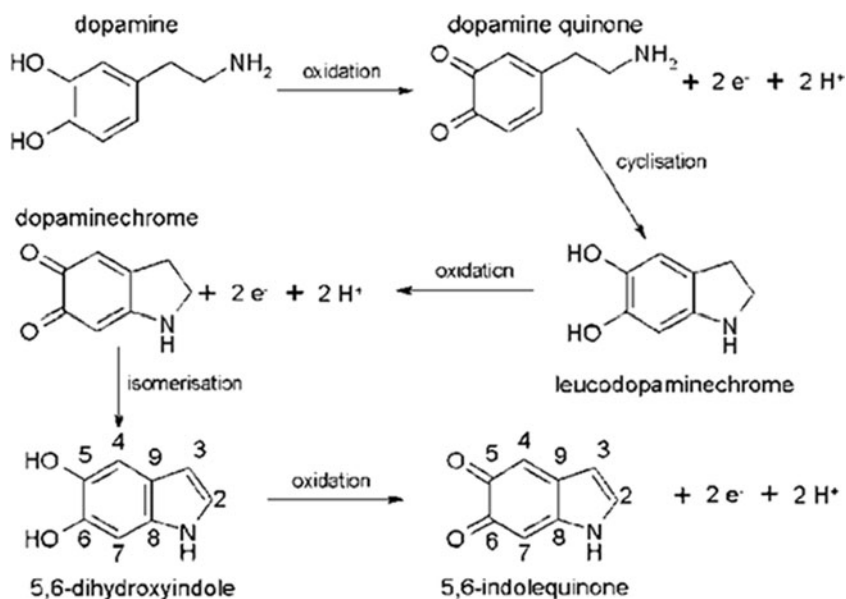
The presence of copper II cations in the films also manifests in spectral changes of the film: Whereas the films produced from oxygenated solutions display the monotonous decrease in absorbance, as expected for melanin in the

framework of the “chemical disorder model” [56], those produced from deoxygenated solutions in the presence of Cu^{2+} display some marked peaks at 370 nm and at 315 nm (Fig. 4b). This may well be related to the influence of Cu^{2+} on the self-assembly of the thin polydopamine films. Indeed, it has been shown by means of small angle X-ray and neutron scattering that Cu^{2+} cations affect the aggregation pathway of synthetic melanin (obtained from tyrosine) in solution [57]. These points remain to be explored in more details to understand the film deposition kinetics in the presence of Cu^{2+} as an oxidant. Anyway, the fact that polydopamine films can be deposited onto substrates even in acidic conditions considerably broadens the potentiality of the obtained films particularly when the substrate to be coated is pH sensitive.

It has also been found that at a given pH value of 8.5 , the nature of the used buffer has a marked influence on the polydopamine film deposition process. In the presence of Tris buffer (50 mM , $\text{pH}=8.5$), the polydopamine film reaches a final and constant thickness of about 45 nm whereas in the presence of phosphate buffer, the film continues to grow up to 100 nm without measurable incorporation of phosphates in the polydopamine film [52].

Complementary to the solution oxidation methods described up to know, it is also possible to produce polydopamine like coatings through electropolymerization in a pH and in an electrolyte-dependent manner [58]. Electropolymerization performed in deoxygenated solutions offers the advantage to allow the restriction of the reaction on the surface of the electrode to be coated, but it has the drawback to be limited on the surface of electrically conducting materials. Another advantage of the electropolymerization is that the maximal film thickness can be reached in about 100 cycles of cyclic voltammetry (scan rate of 10 mV s^{-1}

Scheme 2 Reaction pathway leading to the production of 5,6-indolequinone from dopamine



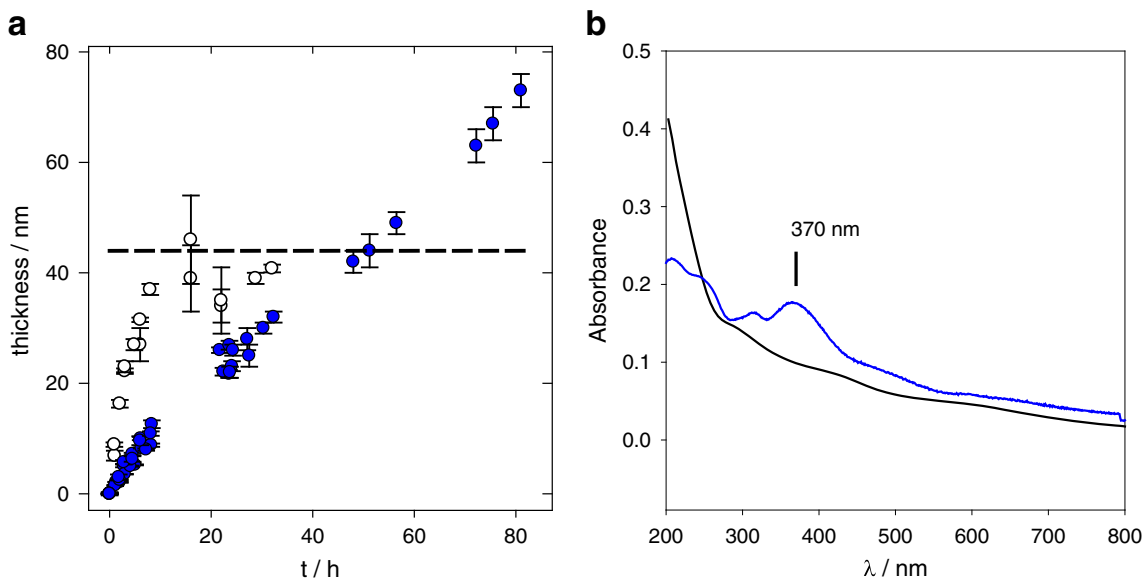


Fig. 5 **a** Thickness evolution with time of “polydopamine” films produced from dopamine solutions (2 mg mL^{-1}) in the presence of oxygenated Tris buffer (50 mM at pH 8.5) (white circle) and in the presence of the same buffer but deoxygenated and in the presence of 30 mM copper sulfate (blue circle). **b** UV-vis spectra of

“polydopamine” films deposited on a quartz slide from oxygenated (black line) or from deoxygenated solutions containing 30 mM copper sulfate (blue line). Adapted from [52] with authorization from the American Chemical Society

between -0.5 and $+0.4$ V versus Ag/AgCl) and in a reaction time of about 3.5 h whereas the same thickness of 45 nm by solution oxidation is only reached in about 15 h [35].

In the case where the polydopamine film is deposited by electropolymerization, the film thickness reaches also a final constant value after which the dopamine in solution cannot further be oxidized. We will explain the origin of this film growth cessation in Section 4. Interestingly this limiting thickness is of 45 nm, the same maximal value reached when the substrate to be coated is put in the presence of an oxygenated dopamine solution at pH 8.5. In this latter case, the maximal film thickness is reached even if there remains a lot of polydopamine grains in solution. This implies that the polydopamine grains do not adhere to the deposited film probably due to electrostatic repulsions. We wondered if the maximal thickness of 45 nm is an absolute limitation of melanin films. Indeed, if polydopamine is a universal, substrate-independent coating methodology, one should be able to deposit polydopamine on a substrate already coated with the same film. Indeed, this works (Fig. 6) provided that the dopamine solution is regularly refreshed [52]. The film can then grow with maximal thickness increments of about 45 nm in each deposition step. These experiments show the importance of dopamine and/or its small oligomers in the deposition process.

A very interesting finding was that dopamine is able to reduce graphene oxide and to stabilize the obtained graphene in solution. This is possible because polydopamine coats the graphene sheets and hence modifies its interactions

with water [59]. Up to now the mechanism by which polydopamine grows from the surface is not well-known. It might well be that the reaction mechanism is similar to that of the deposition of polyaniline, implying the adsorption of radical species from which the growth process occurs. Whatever the details of the deposition mechanism, it is clear

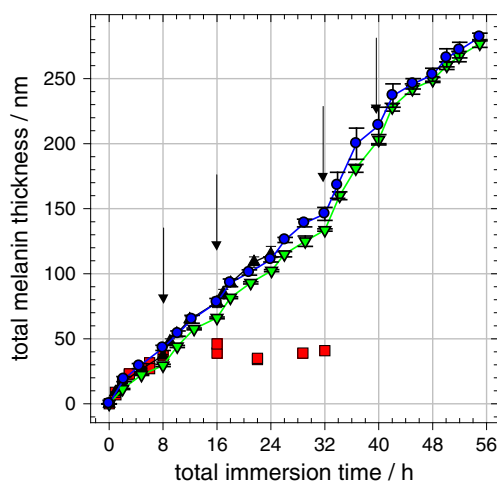


Fig. 6 Thickness of polydopamine coatings on silicon substrates as measured by ellipsometry in the dry state after a single injection of dopamine (2 mg mL^{-1} in the presence of 50 mM Tris buffer at 50 mM) (red square) and after multiple injections of dopamine in the same conditions (blue circle, black triangle, green inverted triangle). Each new injection of a freshly dissolved dopamine solution corresponds to a vertical arrow. Figure modified from [52] with authorization from the American Chemical Society

that small molecular species like dopamine and its oligomers play an important role in the deposition process: When a dopamine solution is oxygenated during 4 h, it is already black but no film deposition is observed when a silicon slide is put in this solution [48].

It should also be pointed out that the molecular details of the self-assembly of melanin in solution are not well-known yet. The basic building block, 5,6-indolequinone (Scheme 2), undergoes dimerization, but there are several isomers or the dimers, three of which being stable enough to contribute to the formation of trimers [60]. This highlights the structural complexity of the obtained melanin. The reactivity of dopamine [61] and of 5,6-dihydroxyindole in solution is a very active research field [62–65] and correlations should be made between this fundamental research in organic chemistry and the surface science of polydopamine deposition. Many theoretical investigations have been performed on the structure of melanin in solution [66], but to our knowledge, not much research has been done toward understanding polydopamine deposition on surfaces. In order to correlate polydopamine formation in solution and on surface, an important point is to know if the basic building blocks are identical in both phases. Owing to the composition and UV–vis spectra (Fig. 4) of the polydopamine films produced in the presence of dioxygen, this is a reasonable assumption.

Quite surprisingly, polydopamine films have not yet been produced from solvents other than water. Based on the results of Lorite et al. [67], it is not unexpected that films produced from dopamine solutions in organic solvents could have other morphologies and structures than those produced in water. Indeed, Lorite et al. evidenced the importance of the presence of water on the film morphology after solvent casting of synthetic melanin. Melanin has been synthesized either in water, in dimethyl sulfoxide (DMSO), or in *N,N*-dimethylformamide (DMF). The root mean squared roughness of the films scaled as a power law of the image size L with a scaling power α . α was found to be much larger (about 0.6) when melanin was synthesized in water than for melanin prepared in DMSO or DMF ($\alpha \sim 0.4$ – 0.45) [67].

As a last point, one may wonder if the interaction strength of polydopamine coatings with the substrate is independent or not from the surface chemistry of the latter. It is well established that the final film thickness obtained in a one-step deposition process (i.e., no fresh dopamine solutions are put in contact with the substrate, see Fig. 5) is almost independent from the substrate [35]. But it would be highly surprising if the adhesion strength of the polydopamine films would not depend on the surface chemistry of the substrate. Indeed, there are recent qualitative experiments relating some spontaneous delamination of the polydopamine films from silicon substrates (Del Frari et al., submitted for publication).

4 Properties of Polydopamine Films

Owing to their composition and heterogeneous structure, polydopamine films should offer a plethora of possible applications in engineering the surface of materials or to modify the surface chemistry of colloids and nanoparticles. In addition, the presence of quinone or catechol groups offers an interesting platform for secondary surface functionalization as was already illustrated in the first papers dealing with the deposition of polydopamine from dopamine solutions [35]. In the last 3 years, the promises of polydopamine coatings have been widely illustrated, as will be shown in the paragraphs below.

4.1 Stability of Polydopamine Films

Polydopamine films deposited on silica were stable in the presence of a physiological buffer for at least 4 days as evaluated by means of ellipsometry measurements. The stability was also excellent at pH 1, and only 14% of film erosion was found within 54 h. But the films spontaneously delaminated within 15 min of exposure to sodium hydroxide solutions at pH 13, most probably due to the pH induced dissolution of the silicon oxide layer covering the silicon slide, but also in relation to the increased solubility of “melanin-like materials” in basic media [48].

4.2 Surface Energy of Polydopamine Films

The most evident consequence of the deposition of a film having a given constant composition ($N/C \sim 0.125$, the same ratio as for dopamine [35, 48]) is the change in the surface energy of the coated material. Indeed, static contact angle measurements on polydopamine films with water as the solvent mostly point to contact angle values of about 50–55° when polydopamine is deposited on hydrophilic substrates [35, 48, 68]. On copper coated with polydopamine, the static contact angle of water also decreased to 50° [69]. On gold, platinum, and indium tin oxide, the static contact angle of polydopamine coatings for water reaches also a constant value of 46–51° after 3 h of contact with a dopamine solution [70]. However, on polyethylene, the contact angle decreases from $127 \pm 6^\circ$ to only $92.8 \pm 1.2^\circ$ after functionalization with polydopamine and on polytetrafluoroethylene the contact angle decreases from $124 \pm 3.4^\circ$ to $80.6 \pm 5.0^\circ$ [71].

When the polydopamine coatings are produced from norepinephrine (Scheme 1), the static contact angle for water is close to 62° on the surface of almost all the coated materials. This may well originate from the influence of the precursor molecule on the composition of the obtained film [36]. Indeed, norepinephrine contains one hydroxyl group more than dopamine (Scheme 1). Polydopamine films can

also be deposited on superhydrophobic surfaces, anodic aluminum oxide covered with fluorosilanes, allowing for a reduction in the static water contact angle from $158.5 \pm 2.8^\circ$ to $37.3 \pm 2.6^\circ$ [72].

The surface energy of polydopamine using the contact angles of droplets made from different solvents (water, diiodomethane, and formamide) has been evaluated [73]. The polar component and apolar components of the surface energy amount to 42.6 ± 1.0 and 18.1 ± 0.9 mJ m^{-2} for poly(L-lactic acid) (PLA) treated with a dopamine solution during 24 h (2 mg mL^{-1} dopamine in 10 mM Tris buffer at pH 8.5), showing that polydopamine coatings are essentially polar and hydrophilic in nature [73].

4.3 Optical Properties of Polydopamine Films

The melanin films produced through spin coating of synthetic melanin from ammonium hydroxide solutions had an extinction coefficient of $3 \times 10^6 \text{ m}^{-1}$ at 589 nm, taking the scattering losses into account through an integrating sphere. The films prepared by oxidation of dopamine using O_2 as the oxidant had an extinction coefficient of $(2.6 \pm 0.4) \times 10^6 \text{ m}^{-1}$ [74] at 589 nm in close agreement with the values obtained by the group of Bothma et al. [38]. The extinction coefficient of the films could be reduced by a factor of two when melanin particles (also produced by oxygen mediated oxidation of a 2-mg mL^{-1} buffered dopamine solution) were deposited on the quartz substrate in a layer-by-layer approach using poly(diallyldimethyl ammonium chloride) as the polycation [74].

Photopyroelectric spectroscopy was performed on electropolymerized melanin films. These experiments allowed to calculate the optical absorption of melanin in the solid state and to estimate an optical gap at 1.70 eV [75].

4.4 Electrochemical Properties of Polydopamine Films

The impedance spectra of polydopamine films produced by successive immersions in dopamine solutions (in a closed vessel) have been measured as a function of the number of the immersion steps of the substrate in the freshly prepared dopamine solutions (2 mg mL^{-1} in the presence of 50 mM Tris buffer at pH=8.5) [76]. From the resistance to electron transfer and taking the film thickness into account, it was found that the conductivity in the direction perpendicular to the melanin films lies between 0.25 and $1.3 \times 10^{-10} \text{ S cm}^{-1}$. This range of values is below those determined for synthetic 3,4-dihydroxy-L-phenylalanine (DOPA)–melanin in the presence of 100% relative humidity, namely $10^{-5} \text{ S cm}^{-1}$ [38, 77]. However, the measurement method used by Jastrzebska et al. [77] was totally different from that used by Ball, namely electrochemical impedance spectroscopy [76]. In addition, the nature of the samples was totally different in these two studies: Jastrzebska et al. [77] used pellets from

melanin powder whereas Ball [76] made his measurements on polydopamine films.

The permeability of polydopamine films to ions depends on the pH and hence on the surface charge of the film, but also on its porosity. Positron annihilation spectroscopy performed on polydopamine films allowed to show that the concentration in organic material was higher at the substrate/film than at the film/solution interface [78]. To our knowledge, no quantitative investigation of the pore size distribution has been performed on polydopamine coatings.

The polydopamine films display a pH-dependent permselectivity: They are positively charged at pH below about 4 [76] and hence display some permeability for anions. Above the isoelectric point, they are permeable to cations [79].

For a given electrochemical probe, the permeability of polydopamine coatings depends markedly on the preparation method. For a given film thickness, the relative oxidation current is higher for films made by electropolymerization than for those made by oxygen bubbling (Fig. 7) [80].

4.5 Electromagnetic Properties of Polydopamine Films

Melanin films produced by spin coating of synthetic melanin from a ammonium hydroxide solution have a conductivity of $2.5 \times 10^{-5} \text{ S m}^{-1}$ at ambient temperature and in the presence of 100% relative humidity [38]. The melanin films produced by spray coating display a decreasing resistance when the temperature increases, a typical behavior of a semi-conductor [37].

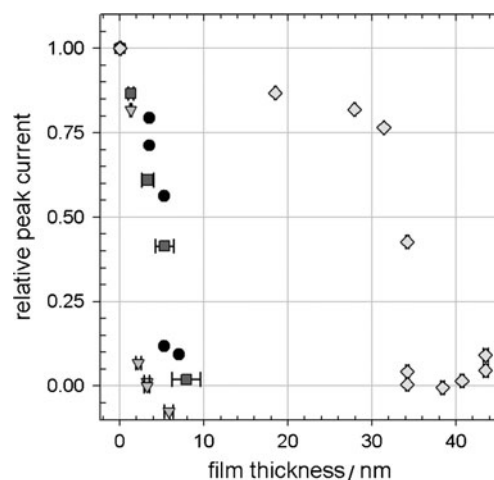


Fig. 7 Relative peak currents of $\text{Fe}(\text{CN})_6^{4-}$ (1 mM in presence of the Tris– NaNO_3 buffer at pH=8.5) versus thickness of melanin deposits on the working electrode obtained by successive immersion in freshly prepared dopamine solution (circles), by continuous oxygenation of a single dopamine solution (triangles), by oxygenation with copper sulfate (squares), or by electropolymerization (diamonds). Each point corresponds to an experiment performed on an independent electrode modified by a polydopamine film. Reproduced from [80] with authorization from Science Direct

Melanin grains display a characteristic signal in electron spin resonance (ESR) due to the presence of semiquinone-like radicals [81, 82]. An almost identical signal is found for polydopamine films prepared from oxygenated dopamine solutions at pH 8.5 [83]. It has been estimated, based on the ESR signal intensity, the film density, and its thickness, that about one over 26 indole quinone group is present in the form of a radical. The strong analogy between the ESR spectra of polydopamine films and those of bulk melanin is an additional strong argument to those proposed in the previous section that polydopamine films may indeed be melanin coatings.

5 Applications of Thin Polydopamine Films

5.1 Polydopamine as Coatings for the Inhibition of Corrosion

The compact and homogeneous nature of polydopamine coatings as well as their permselectivity makes them natural candidates as anti-corrosion coatings. Good resistance against corrosion was observed on copper after coating with polydopamine and its subsequent reaction with 1-dodecanethiol. This two step functionalization of copper made the surface hydrophobic with a static contact for water of 120°. A great part of the corrosion inhibition in the presence of 3.5% NaCl (*w/v*) solutions may hence be due to a lack of direct contact between water and copper [69]. In a similar manner, silicon [84] and aluminum [85] were modified with (3-mercaptopropyl)trimethoxysilane before deposition of the polydopamine film and further modification with tetradecanoyl chloride. Significant improvement in the inhibition of corrosion was found on the surface of these materials.

More research is needed to demonstrate the intrinsic ability of polydopamine coatings to protect the substrates onto which they adhere against corrosion. A step toward this goal will be to investigate the adhesion strength, the stability in time, and the oxygen/hydronium ion permeability of melanin films on variety of different substrates. Up to now, the only studies in which different substrates were compared for the thickness and composition of polydopamine films were reported by Lee et al. [35, 36].

5.2 Polydopamine for Adhesion and Lubrication Improvement

A three-layer coating comprising an intermediate polydopamine layer and an upper layer of stearoyl chloride allowed to obtain excellent tribological behavior on silicon. The intermediate polydopamine layer was assembled on a monolayer of 3-aminopropyltriethoxysilane (APTES) to improve

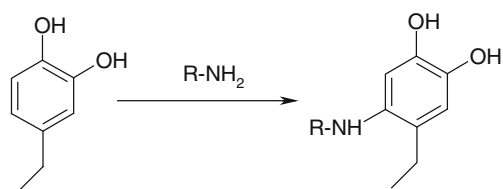
its adhesion to the underlying silicon substrate [86]. Indeed, strong adhesion between the lubricant layer and the substrate is mandatory to ensure stability of the coating under wear. The stearoyl chloride interacted with polydopamine to form amide bonds and the C18 chains made the film hydrophobic in order to improve the tribological properties of the coating. The relative friction coefficient obtained from AFM measurements was decreased by a factor of about 2 for the APTES–polydopamine–stearoyl chloride trilayer with respect to the APTES-functionalized silicon. In a macroscopic ball-on-plate test, the friction coefficient of the APTES–polydopamine–stearoyl chloride trilayer was found equal to 0.2 whereas it was of 0.1 on the APTES–stearoyl chloride bilayer. However, the anti-wear lifetime of the bilayer (i.e., without polydopamine) was only of 50 s whereas it was higher than 3,600 s for the trilayer (i.e., in the presence of the polydopamine interlayer), showing that polydopamine stabilizes the coating [86].

Polydopamine allowed to increase the strength of composite fibers made from PLA platelets and vegetal fibers. The Young's modulus of the composite made from 20% PLA was increased by 5% when PLA was coated with polydopamine before blending with the fibers [73].

5.3 Polydopamine Films for Grafting of Biomolecules

Melanin extracted from living organisms is always found in the presence of proteins [49] owing to the intrinsic ability of catechol and quinone containing materials to form covalent bonds with nucleophilic molecules. The possibility to anchor proteins via their amino groups on the surface of polydopamine films is illustrated in Scheme 3. The reaction between amino groups of proteins and the catechol groups immobilized at the surface, or at the surface of melanin grains in natural melanin, offers the advantage to be a one-step reaction.

The first example of protein binding to polydopamine films has been given by Lee et al. [87]. Their findings were further confirmed by Bernsmann et al. [88] who additionally estimated the specific binding capacity of polydopamine grains produced through the oxidation of dopamine solutions (2 mg mL⁻¹ dopamine in the presence of 50 mM Tris buffer and in the presence of oxygen during 24 h) (Fig. 8).



Scheme 3 The reaction between proteins via free amino groups to the surface of polydopamine functionalized substrates. Inspired from [87]

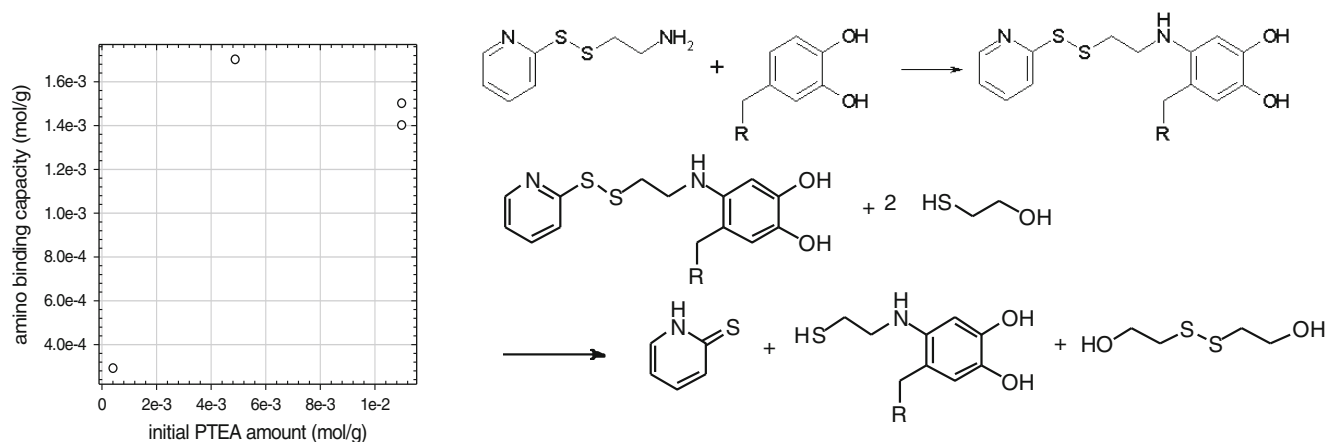


Fig. 8 Use of 2-(2-pyridyl dithiol)ethylamine to estimate the binding capacity of melanin grains for small amino groups. Modified from [88] with authorization from Science Direct

Lee et al. showed that the polydopamine films made from norepinephrine were able to bind trypsin and that the bound enzyme was active to hydrolyze *N*- α -benzoyl-D,L-arginine *p*-nitroanilide [36]. Polyethylene glycol with terminal amino groups could be grafted on polydopamine films in a similar manner to coat the inner wall of capillaries. Such coated capillaries were non-adhesive for proteins allowing to increase the efficiency of their separation in capillary electrophoresis [89]. In a different manner, a polydopamine coating can be used as an adhesive layer for open tubular electrochromatography [90].

Molecules containing thiol functionalities also bind to polydopamine films. This is expected on the basis of the catechol and quinone groups available on the surface of polydopamine [35].

5.4 Composites Based on Polydopamine

The reducing ability of polydopamine coatings allows for the spontaneous reduction of metallic cations, among them silver and iron, as was already demonstrated in the funding paper of Lee et al. [35]. Silver-decorated polydopamine layers constitute seeds for silver plating, and the obtained silver deposit can be sintered at room temperature by simple and rapid contact with electrolyte solutions (CaCl_2 , NaCl , MgSO_4) [91]. The resistivity of the coatings decreases importantly upon treatment with the electrolyte solution, highlighting the efficiency of this sintering method. It has been attributed to coordination of the cations from the electrolyte by the benzoquinone ligands covering the deposited silver nanoparticles, inducing the desorption of the insulating benzoquinone from the surface of the nanoparticles.

The deposition of polydopamine on Fe_3O_4 nanoparticles allowed for further deposition of gold nanoparticles (Fig. 9) and their subsequent functionalization with self-assembled

monolayers ending with iminodiacetic–copper complexes. These core–shell particles were used as specific ligands to fish bovine hemoglobin from complex protein mixtures [92].

Melanin films containing magnetite nanoparticles have also been deposited on Au(111) through electrodeposition of melanin grains (in the presence of 0.1 M NaOH and at -1.0 V versus the saturated calomel electrode). These films allowed for an electrocatalytic reduction of hydrogen peroxide. The electrocatalytic behavior is due to the iron bound to melanin and not to Fe_3O_4 , since the electrocatalytic activity was conserved in neutral or acidic solutions or in the presence of ethylene diaminetetraacetic acid which dissolve magnetite [93].

Graphene sheets modified with polydopamine could easily be decorated with silver particles through polydopamine induced reduction of silver cations [59]. In an identical

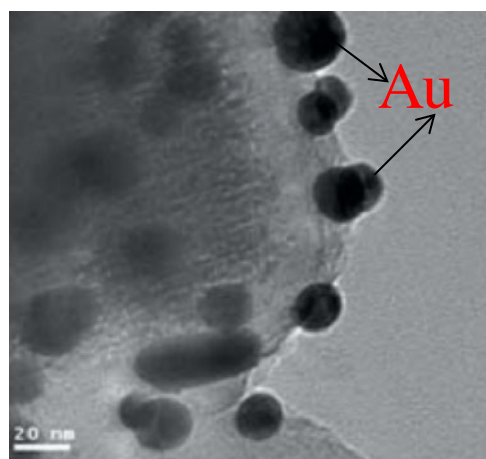


Fig. 9 TEM micrograph of a Fe_3O_4 -polydopamine–Au core–shell particle prepared at Fe_3O_4 -polydopamine/ HAuCl_4 mass ratio of 100/3. Modified from [92] with authorization from the Royal Chemical Society

manner to graphene oxide, carbon nanotubes can be modified in a single reaction step with polydopamine films, and subsequent reduction of AuCl_4^- into gold nanoparticles can be performed [94]. Silver nanowires have also been coated with a polydopamine shell [95].

Many attempts have been made to produce composite materials by associating polydopamine films with other materials to confer the huge potentiality of polydopamine to the obtained composites. The mechanical properties of composites made from vegetal fibers and PLA platelets are improved when PLA is covered with the catechol-rich film [73].

Polyelectrolyte multilayer films made from hyaluronic acid and poly-L-lysine (PLL) were put in contact with buffered dopamine solutions (2 mg mL^{-1} in 50 mM Tris buffer at pH 8.5) and could be detached as free standing black films after oxidation of dopamine and its transformation into polydopamine. Fluorescence recovery after photobleaching allowed to show that the mobility of the PLL chains labeled with fluorescein isothiocyanate was drastically reduced after the formation of polydopamine. The rigidification of the film is ascribed to the formation of covalent bonds between the amino groups of PLL and the catechol groups of polydopamine [96].

Polymers containing DOPA, lysine (Lys), and poly(ethylene glycol) (PEG) were also deposited in a layer-by-layer manner with sodium montmorillonite to obtain rigid membranes having an elastic modulus of $6.8 \pm 0.9 \text{ GPa}$ and an ultimate stress of $200 \pm 28 \text{ MPa}$ [97]. The idea behind this investigation was for an improvement of the interaction strength between the polymer and the clay nanosheets to improve the load transfer in the nanocomposite. The polymer carrying functionalities similar to those of the MEFP5 in mussel was successful to realize this aim. Indeed, reference experiments were performed with the polymer carrying only Lys and PEG: The composite multilayer films had a Young modulus 40% lower than that of the polymer carrying the 3,4-dihydroxy-L-phenylalanine moieties. More spectacular was the four-fold increase in toughness upon the incorporation of DOPA [94]. The crosslinking of the DOPA containing composites was made through a combination of DOPA- Fe^{3+} complexation and autooxidation of DOPA in alkaline and oxygenated media.

Of great interest is the paper by Jaber and Lambert who found that the oxidation of DOPA in the presence of laponite and produces an exfoliation of the clay [98]. In addition, the presence of the clay accelerates the oxidation–aggregation mechanism of DOPA, and at the end, a composite material is produced as shown by thermogravimetric analysis, transmission electron microscopy, and nuclear magnetic resonance spectroscopy [98]. This work may present fascinating possibilities for the production of a new generation of nanocomposites.

5.5 Antibacterial Coatings

When silver is deposited on a polydopamine coating deposited on a cotton fabric, this textile acquires antibacterial properties [99]. In addition, silver nanoparticles (about 50–100 nm in diameter) remain on the surface of the modified fabric for a small number of washing steps. We recently confirmed these results, but we also showed that silver is almost quantitatively desorbed from the polydopamine surface in contact with the *Escherichia coli* containing medium [83]. We then tried, unsuccessfully, to reinitiate the deposition of silver nanoparticles from a silver nitrate solution. The origin of the electrons able to reduce silver cations was asked in this contribution. Electron spin resonance spectroscopy allowed to show that the concentration of free radicals was not affected during silver reduction, suggesting that the paramagnetic species of the polydopamine coating are not at the origin of its reducing ability [83].

Layer-by-layer films made from poly(ethylene imine) modified with catechol groups (PEI-C) and from hyaluronic acid modified with the same moieties can be deposited on substrates like polyethylene or poly(tetrafluoroethylene) which are usually not well suited for electrostatic adsorption. In addition, when such films are put in contact with silver nitrate solutions, silver cations are reduced in metallic silver. This reduction process confers some antimicrobial properties against *E. coli*. [100].

Unfortunately there are no available investigations on the antibacterial and immunological response of pristine polydopamine films. Such investigations should be made urgently owing to the implication of melanin, the probable material of the polydopamine films, in microbial pathogenesis [101].

5.6 Membranes Decorated with Polydopamine—Applications for Separations and in Energy Conversion Processes

The possibility to have a quasi-universal functionalization method should allow to solve one of the major challenges in separation membranes, namely to obtain a robust coating of an active layer, selective enough to afford efficient separations and thin enough not to decrease the permeation flux too markedly. Polydopamine coatings seem to be an ideal candidate to solve this problem.

Indeed, porous polysulfone membranes can be easily modified with polydopamine (Fig. 10). The polydopamine coatings confer interesting permselectivity to the microporous polysulfone membranes. The enrichment factor of thiophene, defined as the ratio between the weight fractions of this solute in the permeate and in the feed compartments, was found to depend on the concentration of the dopamine solution, on the pH of the solution used during the

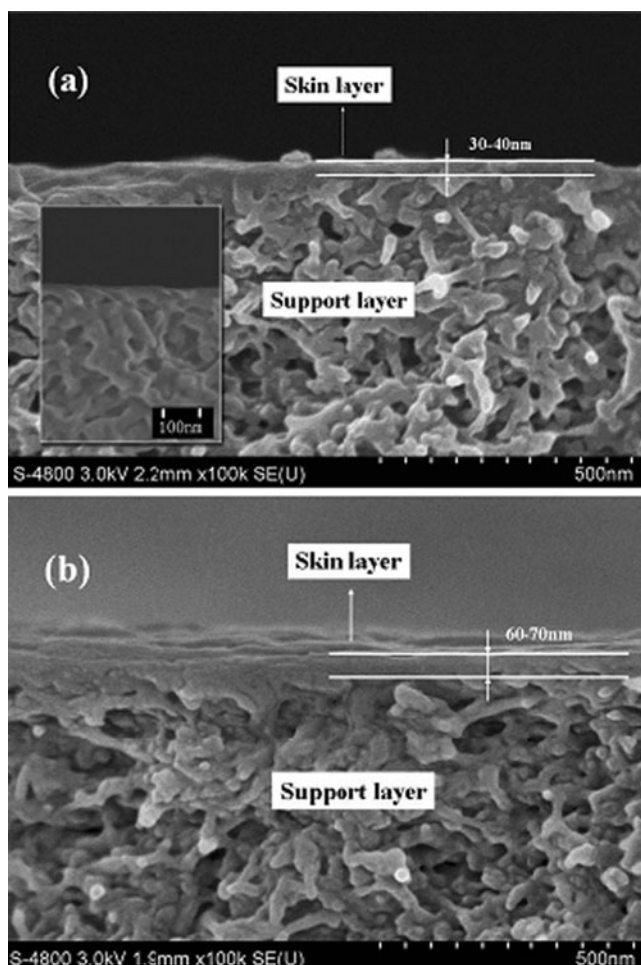


Fig. 10 Scanning electron micrograph of the cross section of a poly-sulfone microporous membrane coated with a single layer (a) and a double layer of polydopamine (b). From [78] with the authorization from the American Chemical Society

deposition [78]. It was found that the permeation flux increased with the initial pH value of the dopamine solution and that the enrichment factor of thiophene decreased with pH in the range from 7.5 to 9.5. These interesting findings are in line with positron annihilation spectroscopy which allowed to show that the porosity of the polydopamine coatings increases with the pH of the dopamine solution used to produce the film [78]. A Nafion membrane used in fuel cells and coated with polydopamine enhances the methanol barrier properties without hindering the proton transport, a property which is mandatory to enhance the efficiency of the methanol fuel cells [102].

5.7 Sensing and Biosensing on Polydopamine-Coated Substrates

The possibility to immobilize proteins on the surface of polydopamine coatings [87, 88] offers numerous advantages as biosensing platforms. It has to be noted that protein

binding not only occurs through covalent binding via Schiff base reaction but that electrostatic interactions also play a role [88].

For instance, the immobilization of antibodies directed against sulfate-reducing bacteria (SRB) on a polydopamine layer allows for the specific detection of these bacteria which reduce sulfate anions into highly toxic and corrosive sulfides [103]. In addition, when the polydopamine film was deposited on a working electrode, the resistance to the transfer of electrons, obtained from the analysis of electrochemical impedance spectra, was a linear function of the number of colony forming units of SRB [103].

Anti-human IgG could be immobilized directly on polydopamine films produced through electropolymerization from a dopamine and anti-human IgG containing solution. These antigens could be recognized by human IgGs put in contact with the film [104]. Moreover, the immobilization of anti-human IgG into polydopamine films was compared to its immobilization in polypyrrole films, and it appeared that polydopamine coatings display a higher density of binding sites to human IgGs than their polypyrrole counterparts [104].

The same group reported the possibility to incorporate active glucose oxidase into electropolymerized polydopamine films. Very interesting was the finding that preoxidized dopamine, due to the presence of potassium ferricyanide in solution, allowed for more efficient immobilization of the enzyme [105]. Nicotine was also imprinted in polydopamine films deposited by electropolymerization in order to produce capacitive sensors specific for nicotine [106].

Concanavalin A (conA) bound to the surface of a polydopamine film can be used to recognize specifically the α -mannose carrying glycoprotein ribonuclease B whereas the α -mannose-deficient ribonuclease A was not bound to the conA-modified polydopamine film. The interaction between the bound lectin and the ribonucleases was investigated in real time by means of surface plasmon resonance spectroscopy and surface-enhanced laser desorption/ionization mass spectrometry [107]. Polydopamine films deposited on indium tin oxide electrodes and decorated with flowerlike gold nanoparticles can be used as sensing platforms for the ultrasensitive detection of analytes (detection limit of 10^{-12} M for rhodamine 6G) in surface-enhanced Raman scattering [108].

Gold nanoparticles/polyaniline/polydopamine conjugates could be immobilized on electrodes and allowed to electrocatalyze the oxidation of ascorbic acid. The device displayed a linear response for ascorbic acid concentrations varying from 1.0×10^{-6} to 1.9×10^{-3} M [109]. Finally, composites between halosite clay nanotubes and polydopamine can interact with $\text{Ru}(\text{bpy})_3^{2+}$ cations to yield an electrochemiluminescent sensing platform [110].

5.8 Polydopamine Films as Substrates to Initiate Polymerization

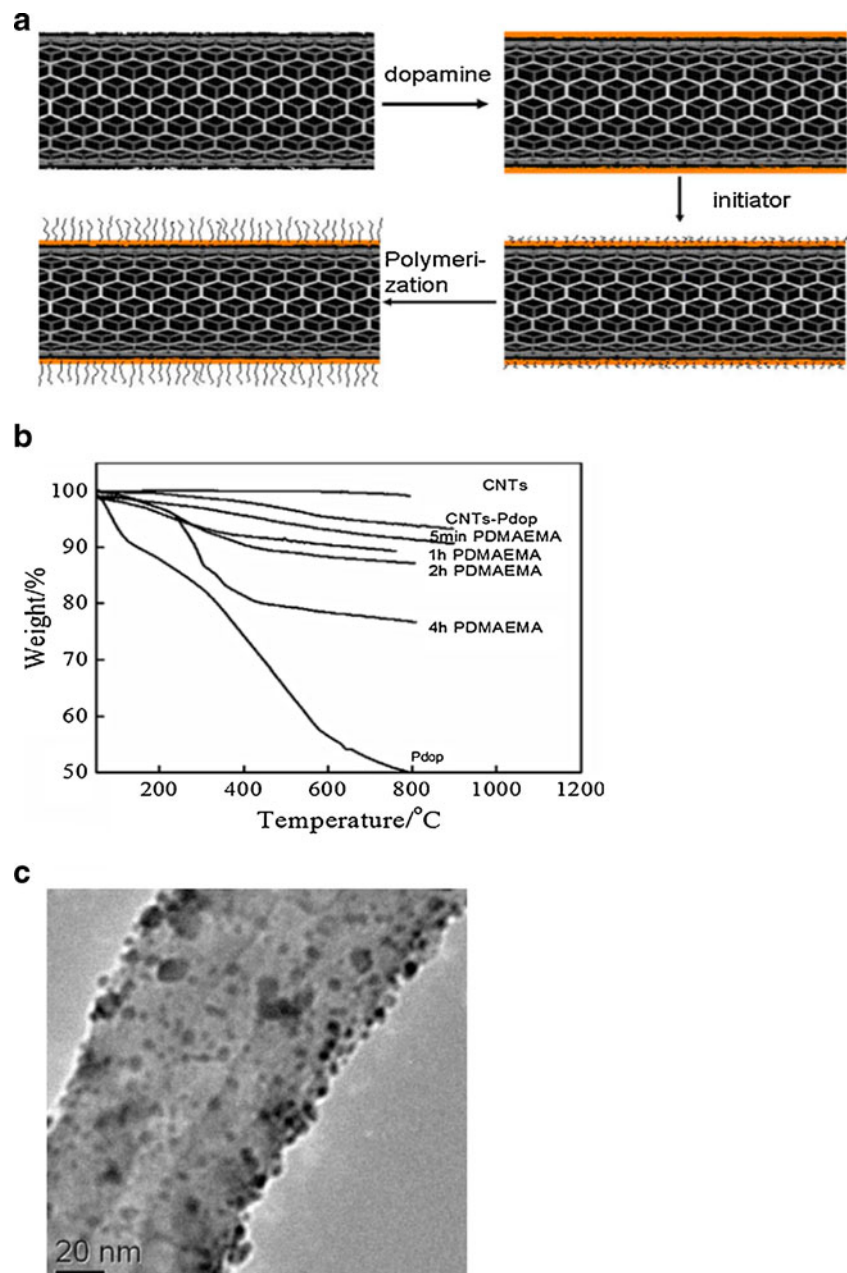
Lee et al. demonstrated that polydopamine layers produced from norepinephrine containing solutions can be used to initiate ring opening polymerization of polycaprolactone. This was possible owing to the presence of alkyl hydroxyl groups on the surface of the films [36].

Zhu and Edmodson demonstrated that it is possible to use polydopamine coatings made from 2-bromoisobutyryl bromide-modified dopamine to grow poly(methylmethacrylate) (PMMA) through an oxygen tolerant variant of atom

transfer radical polymerization. PMMA brushes reached a thickness of 240 nm in 24 h [111].

The surface of carbon nanotubes precoated with polydopamine could also be modified with polydimethylaminoethylmethacrylate (PDMAEMA) brushes through surface-initiated atom transfer radical polymerization (Fig. 11) [112]. The obtained brushes were quaternized with iodomethane and loaded with PdCl_4^{2-} complex anions through an anion exchange process. The metallic cations were finally reduced into Pd nanoparticles (10 nm in average diameter) to obtain an electroactive composite allowing to oxidize methanol.

Fig. 11 **a** Modification of single-walled carbon nanotubes with polydopamine followed with the grafting of polymer brushes. **b** Influence of the PDMAEMA brushes on the thermal stability of the composite nanotubes coated with polydopamine. **c** TEM micrograph of a nanotube coated with polydopamine, quaternized PDMAEMA followed by reduction of PdCl_4^{2-} . From [112] with authorization from Science Direct



5.9 Polydopamine Films as Substrates for Biomineralization

The fact that polydopamine is negatively charged at physiological pH and its ability to interact with metallic cations [53, 54] should offer perspectives in biomineralization processes. Indeed, polydopamine coatings facilitate the precipitation of calcium carbonate from supersaturated solutions. More interestingly, it is the most unstable polymorph of calcium carbonate, namely vaterite, that is deposited and does not reprecipitate in more stable aragonite or calcite [113]. The crystallization of hydroxyapatite on polydopamine films has also been investigated [114]. The addition of biocompatible minerals to polydopamine could offer interesting perspectives for the obtention of fully biocompatible nanocomposites.

5.10 Production of Hollow Polydopamine Capsules

Polymer films have been coated with polydopamine yielding to core–shell composites. When the core is dissolved with a specific solvent, one obtains hollow polydopamine capsules [115–118].

In this kind of capsules, the shell can be deposited in one step which is a major advantage with respect to hollow capsules made through layer-by-layer coating of the core. When the silica particles are put in a basic dopamine solution, the wall thickness reaches 20 nm, significantly lower than the polydopamine film thickness reached on flat substrates (about 45 nm [35]). The obtained capsules did not affect the viability of LIM1215 cells.

Ochs et al. have produced biodegradable capsules by coating silica particles with poly-L-glutamic acid (PGA) modified with dopamine groups. The degradability of the obtained hollow capsules (after dissolution of the silica core) depends markedly on the percentage of dopamine grafting on the PGA chains [118]. At least 15% of the glutamic acid functionalities need to be modified with dopamine to obtain stable capsules after the silica removal. The wall thickness of the obtained shell increases from 7.7 nm when PGA carries 15% of dopamine to 14.7 nm when the dopamine fraction is increased to 25%. Multiple deposition steps of PGA carrying 15% of dopamine groups were possible and allowed for an increase in the capsule thickness. These capsules can be degraded in contact with proteases to release their encapsulated cargo [118]. However, when the degree of PGA modification is equal to 25%, the capsules cannot be degraded anymore.

Porous calcium carbonate colloids were loaded with a first enzyme (α amylase), the composite was covered with polydopamine, and a second enzyme was grafted on the external wall of the polydopamine coating (glucose oxidase). After dissolution of the CaCO_3 core with EDTA, the enzymes kept their activity and allowed to create an enzymatic cascade [119].

5.11 Polydopamine Films as Substrates for Cell Adhesion

The biological applications of polydopamine films have been illustrated in the first original paper describing this surface functionalization method [35]. Since a complete review of this application field is now available [120], we will only focus on the most important findings.

Patterned polydopamine arrays produced by injecting dopamine solutions in poly(dimethylsiloxane) micro-channels allowed the adhesion of various kinds of cells as fibrosarcoma HT1080, mouse preosteoblasts MC3T3-E1, and mouse fibroblasts NIH-3T3 [121]. The blood compatibility of nylon, cellulose, and polyethersulfone decorated with polydopamine films was demonstrated by means of platelet adhesion [122].

The cytotoxicity of core/shell magnetite–polydopamine particles, defined as the ratio between the number of dead cells to the total number of cells, was evaluated and found to be excellent [123]: This finding opens interesting perspectives for the targeting of magnetic particles to specific tissues, the specificity being provided by the biomolecules bound to polydopamine and the toxic Fe_3O_4 being engulfed in the impermeable and stable polydopamine shell.

In the interesting paper by Lynge et al., it was shown that the fluorescently labeled lipids of liposomes covered with a polydopamine film can be internalized by myoblasts adhering on the composite liposome–polydopamine layer [124]. The adhesion of neurons onto polydopamine films is a hot topic owing to the possible implication of melanin in Parkinson's disease [125]. Melanin films made by solvent casting of melanin grains were used to investigate the adhesion of Schwann cells as well as PC12 cells. The obtained coatings had a DC conductivity of $(7.00 \pm 1.10) \times 10^{-5} \text{ S cm}^{-1}$ in the presence of 100% relative humidity, a conductivity value very close to that obtained by the group of Bothma et al. [38]. On melanin films, the growth of Schwann cells as well as the neurite extension was enhanced with respect to reference collagen films [126].

The viability of hippocampal neurons was evaluated on polydopamine films produced from oxygenated dopamine solutions by the live/dead test. The polydopamine coatings were modified with adsorption/covalent binding of poly-L-lysine to improve the cell adhesion. [70]. On the surface of platinum, indium tin oxide, and glass, the cell viability was higher than 30%, a value similar to that obtained on the reference, a glass substrate coated with poly-L-lysine. It was also demonstrated that the polydopamine coating was stable in a biological environment (phosphate buffer at pH 7.4, 5% CO_2 at 37°C) for at least 25 days [70]. The most interesting finding from this investigation was that the adherent hippocampal cells could be stimulated through the polydopamine layer from a gold electrode.

The adhesion strength between *Saccharomyces cerevisiae*, *Bacillus subtilis*, and *E. coli* with polydopamine films has

Table 1 Overview of the main applications of thin polydopamine films

Application field	Comments and main results	References
Inhibition of corrosion	Corrosion inhibition is only efficient if the polydopamine coating is post-modified with a self-assembled monolayer	[69, 84, 85]
Improvement of tribological properties	Polydopamine is part of a three-layer architecture	[85, 86]
Nanocomposites	Coating of nanoparticles, carbon nanotubes Insertion of polydopamine into clays	[92–94] [98]
Grafting of biomolecules and substrates to initiate polymerization	Molecules containing amino and thiol groups bind covalently to polydopamine films in a one-step reaction Polymerization initiators can be bound to polydopamine films to perform RAFT	[36, 87–90] [36, 111, 112]
Antibacterial coatings	Silver ions are reduced in contact with polydopamine and form silver nanoparticles. However, silver is leached in the bacterial suspension and a second reduction step of Ag^+ cations in Ag is not possible	[83, 99]
Membranes for separations and fuel cells	Modification of a polysulfone membrane to make it permselective The permselectivity of polydopamine is pH dependent and also depends on the synthesis method Improvement of methanol barrier in fuel cells	[78] [79, 80] [102]
Films for sensing	Highly selective sensing of an analyte can be obtained by imprinting the molecule of interest in the polydopamine film during its formation	[104–106]
Coating of particles for the production of hollow capsules	Hollow capsules can be obtained in a single-step reaction followed by a removal step of the sacrificial core	[115–119]
Controlled adhesion of cells		[70, 125–127]

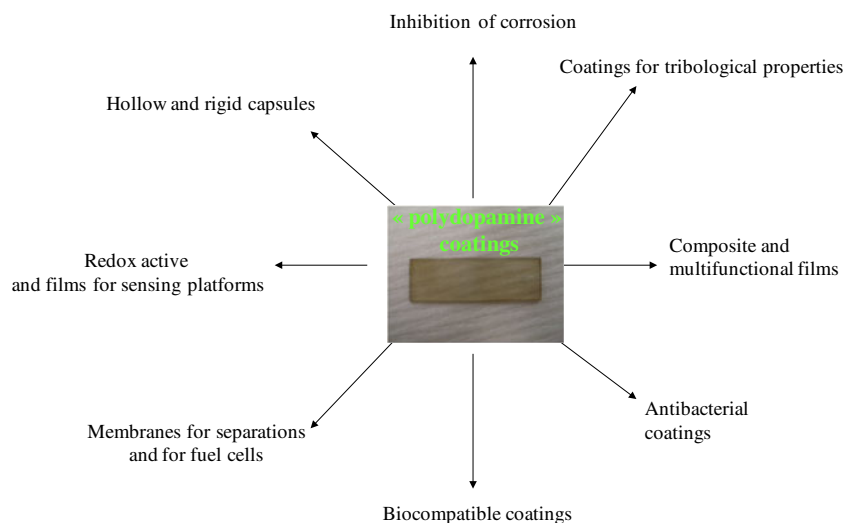
been investigated by means of atomic force microscopy [127]. In the field of biotechnology, yeast cells (*S. cerevisiae*) were encapsulated in a polydopamine coating. They preserved their viability and the cell cycle depended on the thickness of the coating [128]. Such an approach will allow to protect cells from external stresses in a “bacterial spore”-like manner. Interestingly, the polydopamine shell did not prevent the yeast cells from the dividing: It just increased the quiescent phase before cell division. The lag phase preceding cell division depended on the thickness of the polydopamine layer. In addition, polydopamine retarded the digestion of yeast by lyticase [128]. The polydopamine-coated yeast could be easily coated with avidin allowing for a specific adhesion of the cells

on patterned surfaces modified with biotin on specific locations [128]. All these possible applications of polydopamine films are summarized in Table 1 and Scheme 4.

6 Conclusions and Outlook

Polydopamine coatings (certainly made of melanin) constitute a fascinating new surface functionalization method. The polydopamine film deposition can be a one-step process (but it can also be extended to multiple deposition steps, allowing to produce very thick coatings) performed in environmentally friendly conditions and

Scheme 4 Survey of the already explored application domains of polydopamine films. The picture corresponds to a polydopamine film deposited on a quartz slide from a 2-mg mL^{-1} dopamine solution in the presence of 50 mM Tris buffer at pH 8.5. Air was bubbled in this solution during 24 h



with high versatility since almost all known materials, even superhydrophobic perfluoroalkane decorated materials, can be coated. As another major advantage, polydopamine can easily undergo secondary modifications since its catechol and quinone moieties can react with nucleophiles (amines, thiols). In addition, a lot of redox processes can be undertaken, only those leading to the reduction of metallic cations having been explored up to now. These possibilities have led to interesting applications in very diverse fields, as in separation membranes for fuel cells and for cell adhesion purposes for which the known biocompatibility of catecholamines was a natural candidate. Hence, the broad range of applications of polydopamine films (Scheme 4) in addition to the almost independent nature of the substrate to be coated makes polydopamine one of the most promising coating technologies for real-life applications.

Many efforts have to be devoted in the future to make benefit from the optical properties of polydopamine and to combine them with electroactive and photoactive materials like electrochromic and photochromic materials. Such research effort would allow to produce biocompatible composites of high added value and stimuli sensitive coatings.

The ability to produce films having a composition close to that of the *Substantia nigra* of the central nervous system may offer interesting possibilities to investigate the fate of neurons in conditions near to pathological ones. We also anticipate that polydopamine coatings could offer nice opportunities when coupled to stimuli sensitive polymers as well as for the obtention of a new generation of nanocomposites.

Nevertheless to reach such goals, much effort is necessary to explain the deposition mechanism of polydopamine. The most challenging questions will be to understand:

1. The first steps of the deposition mechanism, whose in which the first oligomers of 5,6-dihydroxyindole bind to the substrate
2. Why the thickness of the polydopamine film reaches a limiting value of 45 nm when oxygen is the oxidant and why different thickness growth rates and limiting thickness values are reached when different oxidant (Cu^{2+} for instance) are used
3. Why polydopamine deposition can occur in acidic media in the presence of oxidants like periodate or persulfate

Great progress in the surface science of polydopamine films will be obtained if this community will collaborate closely with researches implied in the fundamental mechanisms of oxidation–aggregation processes of catechols as well as with biologists implied in the processes of melanogenesis. A combined experimental–computational approach could be a powerful method to advance this field.

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