



Polydopamine films and particles with catalytic activity



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ABSTRACT

Coatings obtained from the oxidation of catecholamines, most often dopamine, allow not only to coat the surface of all classes of known materials (metals, oxides, polymers, liquid/liquid and liquid/air interfaces) with a conformal and robust film but also to easily post-functionalize such coatings with metal nanoparticles and enzymes using the intrinsic redox and quinone functionalities of the coating. Hence polydopamine (PDA) based coatings offer huge perspectives for the immobilization of catalysts. This review provides a summary of the first successful research efforts in this domain and provides some first proofs of concept that PDA may act as a catalyst by itself for aldolations, formation of carbonates from CO₂ and epoxides and for hydrolysis reactions without addition of further enzymes or metal nanoparticles.

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1. Introduction

Sensing of analytes in the atmosphere and in water is one of the central aspects for the protection of humans against environmental hazards and pollutants. A considerable research and development effort is devoted worldwide for such applications. The design of sensors is challenging because the obtained devices need [1].

- (i) to be specific for a given analyte in the presence of other molecules that could interfere with the detection.
- (ii) to be sensitive; ie characterized by an as low as possible detection and quantification limit (depending on the noise level of the detection system).
- (iii) to be reproducible and accurate over an as large as possible dynamic range in the analyte concentration.
- (iv) to be reusable for many assays.
- (v) to be stable for a long duration.

Owing to the intrinsic low conformational stability of enzymes, challenges (iii) and (iv) may be difficult to overcome. The catalytic sites on nanoparticles can also be poisoned decreasing progressively the efficiency of the nanoparticles based sensor.

If the sensors use an electrochemical or gravimetric detection system, the sensing molecules need to be immobilized on a solid substrate. In addition, the immobilization of enzymes or of

catalytic nanoparticles on solid surfaces offers major advantages with respect to solubilized enzymes/nanoparticles in performing biosensing assays because the enzymes/nanoparticles can be easily separated from the unreacted substrates and from the obtained products just by a rinsing process [2]. On the other hand free enzymes/nanoparticles in solution need to be centrifuged at high speed and for long durations to separate them from the reactants. Such a process induces an unavoidable loss of catalytic material and reduces dramatically the reusability of the sensing units.

However, the immobilization of enzymes on solid substrates has to be designed in a manner not to change their conformation in a significant manner and to orient their active site in a way to be accessible to the solubilized substrate. This is a particular challenging task because proteins in general and enzymes in particular are characterized by a small conformational stability: the free energy difference between the native fully active state and the fully unfolded and inactive state is often only a few kTs per molecule [3]. The catalytic nanoparticles need also to be grafted on the solid substrate using specific chemistry most often using the capping agents introduced on their surface to stabilize them against colloidal aggregation. These processes are highly specific and a different kind of chemistry has to be used on each class of materials.

The occurrence of a versatile coating method able to mask the specificity of the substrate chemistry and to afford chemical moieties for secondary functionalization is therefore welcome to design new biosensors and catalytic materials based on grafted enzymes and/or nanoparticles. Since 10 years such a versatile coating methodology is available. It was inspired by the chemistry used

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by mussels to adhere to the surface of stones and wood in wet conditions and under strong shear stresses [4]. Mussels adhere through solid substrates through a series of byssus threads the extremity of which is rich in so called *mefp* (Mytilus Edulis Foot Proteins) proteins. Those proteins constitute a family (*mefp* 1 to *mefp* 6) and are characterized by an unusually high content in L-lysine and in L-Dopa (the hydroxylated derivative of the natural amino acid L-tyrosine). It has been shown that the presence of these two amino acids allows for strong adhesion of the mussel to solid substrates [4]. Catecholamines contain the 1,2 dihydroxy benzene as well as the primary amine functions present respectively in L-Dopa and in L-Lysine. Thus they were believed to constitute natural candidates to mimic the adhesion behaviour of *mefp* proteins. Indeed, when dopamine is solubilized in a slightly basic and oxygenated solution it undergoes oxidation resulting in the precipitation of amorphous aggregates in the solution and in the formation of a black conformal coating on the surface of the reaction vessel as well as on the surface of all kinds of substrates put in this solution [5]. In this short review, it will be described how polydopamine (PDA) coatings and related catecholamine based films can be used as platforms for the immobilization of enzymes and catalytic nanoparticles. It will be shown that owing to the presence of redox moieties on the surface of PDA, some metal nanoparticles can be grown directly on the surface of PDA functionalized surfaces by direct contact with a metal cation containing solution. This will appear of the highest interest because it may allow to synthesize the nanoparticles in-situ, to protect them from aggregation before performing catalysis. To explain such an additional versatility for performing secondary functionalisation with either enzymes or nanoparticles, the basic knowledge acquired on PDA films during the last ten years will be summarized in the first part before describing the immobilization of enzymes and nanoparticles on PDA. The last part of the review will focus on an emerging and fascinating concept: the fact that PDA films can display some catalytic activity by themselves.

2. Deposition of polydopamine films

When a catecholamine containing solution is dissolved in a basic aqueous solution, the oxygen spontaneously dissolved in water is a strong enough oxidant to oxidize catecholamines. In the particular case of dopamine, the oxidation process leads to the formation of dopaminequinone which rapidly undergoes cyclisation through a Michael type cycloaddition. [6] This species undergoes additional oxidation to yield finally 5,6 dihydroxyindole (DHI), the building block of eumelanins and also of PDA [7]. From this stage on there are many proposed chemical pathways leading to PDA (Fig. 1) but no definitive proof in favour of one or the other mechanism has yet been given. The proposed mechanisms are:

- (i) The formation of a linear polymer through 4–7' coupling of DHI [8].
- (ii) The obtention of a material made from covalent bonds as well as DHI-dopamine clusters [9].
- (iii) The self-assembly of small oligomers of DHI via π - π stacking and H bonds [10–12].

This last assumption seems to be corroborated, but not definitively proven, by matrix assisted laser desorption ionization mass spectrometry showing the predominance of tetra and pentamers of DHI in eumelanin like materials [13].

Clearly much research efforts have to be devoted in the elucidation of the structures-properties relationships of PDA. The best way may be to recognize the evident analogy between PDA and eumelanin [6,7], the black-brown pigment from the skin and the

eyes and to benefit from the huge expertise of dermatologists in this field.

The deposition of PDA on the surface of solid substrates, not only planar but also colloidal templates [14] is very easy to perform and this fact hides the complexity of the chemical events occurring in the solution [15] (with the final occurrence of precipitation) and on the surface of the substrates immersed in that solution. Indeed the term PDA is certainly not well suited because there may be as many different PDA structures and hence properties as different reaction conditions [16]. It has been shown that a single change in the nature of the buffer molecule at constant pH value and using O_2 as the oxidant changes not only the kinetics of PDA film growth [17] but also the aggregation of PDA in solution and its paramagnetic properties as probed by electron spin resonance spectroscopy [18]. Most of the published articles in this field use the synthesis methodology initially proposed by Lee et al. [5] using the oxidation of dopamine by dissolved O_2 at pH = 8.5 in the presence of Tris (Tris(hydroxymethyl) aminomethane) buffer. But this amine based buffer strongly interacts with the quinone groups present on 5,6 indolequinone and its small oligomers via nucleophilic additions [18]. In addition, plenty of other oxidants than O_2 can be used to produce PDA related materials and coatings from dopamine [19–21]. This is extremely convenient because the presence of dissolved O_2 in basic solutions does not allow to well control the first seconds of the dopamine oxidation process which starts immediately when the dopamine powder is introduced in the solution. However when dopamine is dissolved in solutions with a pH lower than about 6, its spontaneous oxidation is extremely slow and the oxidation-self assembly rate is then under the control of the added oxidant. In addition since O_2 is consumed during the reaction, its concentration is replenished from the water/air interface where the deposition of PDA is faster than in the bulk of the solution: overall the PDA films produced in the presence of O_2 are heterogeneous with a gradient of decreasing thickness from the part of the substrate close to the water/air interface to the parts of the substrate in the deeper part of the aqueous solution [22]. In slightly acidic media, oxidants like sodium peroxodisulfate ($Na_2S_2O_8$) and sodium periodate ($NaIO_4$) allow to produce PDA films with much higher thickness than in the presence of O_2 at pH = 8.5. Note that the limiting thickness of 40–45 nm in the presence of O_2 at pH 5.8 [5] can be easily overcome by an increase in the initial concentration in dopamine but at the prize of a much higher film roughness [23]. An increased roughness may be advantageous for future applications in the immobilization of catalysts on such films. In the case of $NaIO_4$ at an initial concentration of 20 mM and in the presence of dopamine at 10.6 mM, a thickness of 80 nm is reached in 1 h. Such a fast deposition kinetics reflects a fast oxidation process in solution leading almost exclusively to the formation of dopaminochrome, a well known precursor for eumelanin related materials [7]. The surface analysis of the PDA films obtained in the presence of $NaIO_4$ reveals a totally different composition and structure than the PDA films obtained in the presence of O_2 at pH = 8.5 (in the presence of Tris buffer) (Fig. 2). In particular, X-ray photoelectron spectroscopy, infra-red (Fig. 2A) and ^{13}C NMR spectroscopies (of the PDA powder collected in solution), reveal that PDA- $NaIO_4$ contains carboxylic acid functionalities, originating most probably from the oxidative cleavage of dihydroxyindole units (Fig. 2B). As a consequence of the presence of carboxylic acids at the surface of PDA- $NaIO_4$ films they are superhydrophilic whereas PDA films produced from O_2 at pH = 8.5 are only moderately hydrophilic (with static contact angles for water around 40–50°) [5,24].

This finding reflects the previous statement that there are probably as many PDA films and materials than experimental parameters used to get them. This reflects the many chemical pathways occurring in parallel after the initial oxidation of dopamine,

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