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Degradation of polydopamine coatings by sodium hypochlorite: A process depending on the substrate and the film synthesis method

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ABSTRACT

Polydopamine coatings are promising new versatile coatings able to be deposited on almost all kinds of materials. Such films synthesized either by oxygenation or by electrochemistry on indium tin oxide (ITO) and glassy carbon substrates, were degraded by an oxidizing sodium hypochlorite solution. Films were successively immersed in a sodium hypochlorite solution (1 g/L) during different times. The characterizations of film degradation were made by XPS spectroscopy and AFM. They confirmed a homogeneous degradation of polydopamine, due to an oxidation reaction. The influence of the synthesis method and the nature of the substrate on the polydopamine degradation were also studied in this paper: coatings deposited on ITO by oxygenation degrade much faster than those deposited on glassy carbon or by electrochemistry. This suggests that the adhesion of the polydopamine films and their stability is markedly dependant on the used substrate (ITO *vs.* glassy carbon) as well as on the deposition method (oxygenation *vs.* electrochemistry), whereas the film thickness reached during deposition is almost substrate independent.

1. Introduction

Fast and versatile coating technologies are required to protect the surface of materials against degradation events like corrosion or to confer to those materials some new surface functionalities. These new functionalities will allow for secondary chemical grafting reactions to be performed or to change the wettability or adhesive behavior of that material. For a coating method to be versatile it should be applicable on a large variety of materials, like noble metals, oxides and polymers, and preferentially the deposition should be performed in a cost effective manner and in environmentally friendly conditions, preferentially from an aqueous solution. Coating methods which fulfill simultaneously all these criteria are very rare with the notable exception of films having a composition and properties very close to those of melanin, the natural pigment and photoprotectant of the skin [1]. These films can be produced from solutions containing a catecholamine like dopamine [2] or norepinephrine [3] in basic aqueous solutions in the presence of dissolved oxygen which acts as an oxidant. The obtained coatings form films on almost all kinds of materials, even on teflon and on superhydrophobic substrates [4] in a one step manner. The thickness of the polydopamine coatings can be controlled by playing on the reaction time, on the nature of the used oxidant [5], on the buffer used to control the pH of the solution [6] and on the concentration of dopamine [7]. Additionally, it is also possible to deposit polydopamine coatings on conductive substrates by means of electropolymerization [8]. This deposition method can only be applied on surfaces of metals or carbonaceous materials but it offers the advantage to be selective on the surface of the materials were the oxidation of the catecholamine takes place without oxidation in solution. Polydopamine coatings have a composition very close to that of eumelanin, a fascinating heterogeneous biomaterial [9]. They offer the advantage of easy post functionalization with molecules containing nucleophilic groups like thiols [2] or amines [10]. In addition, polydopamine coatings contain free radical groups, as natural melanin does, and sufficient chemical groups allowing to be oxidized and to simultaneously allow for the reduction of metal ions from solution and their subsequent deposition as nanoparticles [11]. In the case of polydopamine films decorated with silver nanoparticles, the obtained coatings display long term antimicrobial properties [12]. Among a plethora of possible applications, which have been reviewed recently [13,14], it has to be cited that polydopamine coatings can be used for the protection against corrosion and that they display a pH dependant permselectivity for ions [15] in accordance with their pH dependant surface potential [16].

Since melanin displays photoconductivity and antioxidative properties, it is of the highest interest to investigate its stability with time and in response to strong oxidants. The investigation of

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such degradation processes can be complicated from natural melanin, particularly due to the presence of proteins. The possibility to have melanin-like coatings on flat substrates allows to investigate such degradation processes in real time with the aid of surface sensitive analytical tools. In addition it is also mandatory to optimize cleaning methods of substrates coated with polydopamine films in order to regenerate the surface of such coatings. Since the adhesion and stability of polydopamine coatings may be dependent on the nature of the used substrate as well as on the used deposition method, it is the aim of this article to investigate the degradation of polydopamine coatings on two different substrates: indium tin oxide (ITO) and glassy carbon electrodes. These two substrates are conductive and well suited for the electrochemical deposition of polydopamine as well as for the following of film degradation by means of cyclic voltammetry. Indeed upon film degradation in the presence of a strong oxidant, as sodium hypochlorite, we expect that the permeability of the polydopamine coating will progressively increase. In addition ITO can be used as a substrate to follow the film degradation by means of X-ray photoelectron spectroscopy (XPS). Indeed, polydopamine films are black [17] and their absorbance will progressively decrease upon film degradation. Some clues into the film degradation mechanism will be obtained from atomic force microscopy (AFM) and XPS in order to investigate the change in film morphology and in chemical composition, respectively, during its degradation. Complementary, we will investigate, on the two substrates (ITO and glassy carbon), the influence of the deposition method, either via oxygenation of dopamine solutions or their electropolymerization, on the degradation kinetics in the presence of sodium hypochlorite. This oxidant was chosen because it is a major constituent in many cleaning and sterilization formulations. At purpose, we used two models substrates for the electrodeposition of polydopamine: glassy carbon and ITO, because they are of broad industrial use in microelectronics for instance.

2. Materials and methods

2.1. Substrates, synthesis and degradation

A summary of the used substrates, their dimensions and the cleaning protocol applied before the deposition of polydopamine are presented in the Table 1.

All solutions are prepared using ultrapure water from a Milli Q Plus water purification system (Millipore, Simplicity). The pH of the solutions is measured with a Mettler-Toledo pH-meter and adjusted by addition of hydrochloric acid solution (37%, Sigma Aldrich) or sodium hydroxide pellets (extra pure, Acros Organics). All experiments are performed at room temperature. Two methods are used to build melanin deposits from aqueous dopamine solutions: melanin formation is initiated by dopamine oxidation either by oxygen or by electrochemistry, as described in reference [18].

In the first method, by oxygenation, the substrate is immersed in a dopamine solution (2 g/L) in 50 mM tris(hydroxymethyl)-aminomethane ($C_4H_{11}NO_3$, UltraPure, Euromedex), at pH = 8.5, continuously aerated with an aquarium pump (Rena Air 50, Mars Fishcare).

In the second method, by electrodeposition, the electrolyte is a dopamine solution (0.5 g/L) in 10 mM tris(hydroxymethyl)-aminomethane, at pH = 7.5. This solution was purged with N_2 during the whole duration of the experiment. The electrochemical potentials of the working electrode was measured and expressed by reference to an Ag/AgCl electrode and the counter electrode was a platinum grid. The experiments were realized using a PARSTAT 2273 potentiostat/galvanostat (Princeton Applied Research). The coating process was realized by a voltamperometric technique. 100 cyclic voltammetry (CV) cycles were applied between −0.4 and 0.3 $V_{/Ag/AgCl}$, at a scan rate of 10 mV/s [8].

After their synthesis, polydopamine films deposited on glassy carbon or ITO were immersed in a sodium hypochlorite solution (NaClO) during a predetermined time. Preliminary experiments have defined an optimum concentration of sodium hypochlorite equivalent to 1 g/L allowing for a fast degradation of polydopamine. A fast cleaning of the substrates is mandatory for practical applications. The hypochlorite ion, ClO^-, is well-known for its oxidative properties and it reacts following this equation:

$$ClO^- + 2H^+ + 2e^- \rightarrow Cl^- + H_2O \quad (1)$$

with a standard redox potential of 0.81 V *vs.* the normal hydrogen electrode. After immersion, the substrates are immediately rinsed with ultrapure water.

2.2. Characterization techniques

Electrochemical characterizations were also made by the cyclic voltammetry (CV) technique. A CV cycle was realized between −0.1 and 0.6 $V_{/Ag/AgCl}$, at a scan rate of 50 m V/s. For these experiments, the electrolyte is a solution of potassium hexacyanoferrate trihydrate at 1 mM (Sigma Aldrich) containing sodium nitrate at 0.15 M (Sigma Aldrich) and tris(hydroxymethyl)-aminomethane at 50 mM (Euromedex), at pH = 7.5.

The Atomic Force Microscopy (AFM) topographies of the films were acquired in the tapping mode with a Pico SPM microscope (Molecular Imaging) at a frequency of 1 Hz. Each image, with a resolution of 512 × 512 pixels, was acquired with a new pyramidal silicon tip.

X-ray photoelectron spectroscopy (XPS) analyses were performed with a Hemispherical Energy Analyzer SPECS (PHOIBOS 150) employing a monochromatic Al Kα radiation (1486.74 eV) operating at 200 W with an anode voltage of 12 kV. The pressure in the analysis chamber was equal to 10^{-9} mbar. The pass energies were set to 80 eV and 20 eV for survey and higher resolution scans, respectively. The binding energy scale was calibrated from the carbon contamination using the C1s peak at 284.6 eV. Core peaks were analyzed using a nonlinear Shirley-type background. The peak positions and areas were optimized by a weighted least-square fitting method using 70% Gaussian and 30% Lorentzian line shapes.

Table 1
Nature, dimensions and cleaning of substrates. 1: CH Instruments, Austin, Texas, USA, CHI 104. 2: Indium tin oxide (glass slides for MALDI imaging – conductive ITO coating), Bruker.

	Nature	Size	Cleaning
Coating	Glassy carbon [1]	0.2 cm^2	Polishing (1 μm): γ-alumina powder with a particle diameter of 50 nm (Buehler, Lake Bluff, Illinois, USA)
	ITO [2]	8 cm^2	Ethanol in an ultrasonic bath during 10 min
AFM	ITO [2]	/	Ethanol in an ultrasonic bath during 10 min
XPS	ITO [2]	/	Ethanol in an ultrasonic bath during 10 min

3. Results and discussion

3.1. Degradation of films produced via oxygenation on ITO and on glassy carbon

Polydopamine films were deposited on glassy carbon and ITO substrates, according to the oxygenation method, the reaction time being equal to 24 h, a time duration sufficient to reach a maximal thickness value of about 40 nm in these conditions (2 g/L in dopamine) according to the literature [2].