Journal of Colloid and Interface Science 386 (2012) 366–372

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Kinetics of polydopamine film deposition as a function of pH and dopamine concentration: Insights in the polydopamine deposition mechanism

Vincent Ball [*], Doriane Del Frari, Valérie Toniazzo, David Ruch

Advanced Materials and Structures, Centre de Recherche Public Henri Tudor, 66 rue de Luxembourg, L-4002 Esch-sur-Alzette, Luxembourg

ARTICLE INFO

Article history:
Received 23 May 2012
Accepted 10 July 2012
Available online 20 July 2012

Keywords:
Polydopamine films
Surface characterization
Kinetics of film formation
Impedance spectroscopy
Rate equations

ABSTRACT

The formation of “polydopamine” thin films becomes a popular method to confer multifunctionality to solid–liquid interfaces through the available catechol groups of such films. The mechanism of film formation is, however, not well elucidated, and most investigators use the protocol developed by Messersmith et al. (H. Lee, S.M. Dellatore, W.M. Miller, P.B. Messersmith, *Science* 318 (2007) 426.) using a dopamine solution at a constant concentration of 2 g L^{-1} in the presence of Tris(hydroxymethyl aminomethane) at pH 8.5. A particular finding of this initial study was that the film thickness reaches a constant value (almost substrate independent) of about 40 nm. Herein, we investigate the change in the polydopamine film thickness, morphology, surface energy and electrochemical properties as a function of the concentration of the dopamine solution put in the presence of silicon substrates. As a surprising finding, we observe a constant increase in the maximal film thickness with an increase in the dopamine solution between 0.1 and 5 g L^{-1}. The surface morphology is also markedly affected by the concentration of the dopamine solution, whereas the different components of the surface energy stay unaffected by the dopamine solution concentration. In addition, electrochemical impedance spectroscopy shows that the higher the initial dopamine concentration, the more rapidly compact and impermeable films are formed. Finally, we propose a model for the deposition of polydopamine films taking all our findings into account. This model relies on a rate equation taking into account both attractive and repulsive interactions between small polydopamine aggregates on the surface and in solution.

1. Introduction

Among the available surface functionalization methods performed in the wet state, only very few allow for the formation of a functional and uniform coating on a large variety of substrates in a single step reaction. The deposition of polydopamine films from a basic solution of dopamine in the presence of oxygen belongs to such methods. Polydopamine films can be deposited on almost any substrate yielding a coating of about 40 nm in thickness after about 15 h of immersion in an aerated and slightly basic (pH = 8.5) dopamine [1] norepinephrine [2] or L-DOPA [3–6] solution. The chemistry of polydopamine formation was originally inspired from mussels (*Mytilus Edulis*) Foot Proteins (MEFPs) that make use of the oxidative polymerization of catecholamines [7,8].

Polydopamine films can also be deposited on the surface of colloidal particles allowing to produce hollow capsules after selective dissolution of the colloidal core [9,10]. This one step coating offers many advantages with respect to the production of hollow capsules made through the deposition of polyelectrolyte multilayer films, among them a better control over permeability. Polydopamine hollow capsules or films have also a pH dependent permselectivity [11]: owing to their negative surface charge density at pH higher than about four [12], they allow for the permeation of cations, whereas they become selective for anions in acidic media having a pH lower than the isoelectric point of polydopamine. Polydopamine films have been found promising candidates for the protection against corrosion [13,14], for promoting biomineralization processes [15,16], for the reduction in friction coefficients [17] for many bio-applications [18], for the functionalization of superhydrophobic coatings [19] and the functionalization of microfluidic devices [20]. Such coatings, having a surface composition similar to that of melanin and often called pseudo-melanin, can also be easily modified in a single step reaction with molecules containing nucleophilic groups such as amines [21,22] or thiols [1] as well as other chemical functionalities [23], or with metal nanoparticles as silver [24] or gold [25] via the reduction of the corresponding cations dissolved in solution. This reduction step may be possible through the presence of catechol groups that undergo an oxidation in quinone functionalities during the reduction of the metallic cations [26]. In addition, polydopamine films can be used to initiate surface induced polymerizations [2,27]. A more detailed description of the applications of polydopamine coatings can be found in a recent review article [28].

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[*] Corresponding author.
E-mail address: vincent.ball@tudor.lu (V. Ball).

0021-9797/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2012.07.030

Surprisingly less effort has been devoted to the investigation of the mechanisms allowing for the deposition of polydopamine films than to their use as active coatings. Such fundamental investigations are mandatory to further improve the properties of polydopamine coatings. In the presence of oxygen as an oxidant, polydopamine is not only depositing on the substrate to be coated but also formed in the solution. When the particles produced in solution are put in contact with an identical substrate, silicon, no film deposition occurs suggesting that the presence of unoxidized dopamine or small oligomers thereof are necessary in the deposition process [29]. A deposition mechanism analogous to that allowing for the deposition of polyaniline from an aniline containing solution has been suggested but not yet demonstrated [29]. Other insights have been given on the deposition mechanism through the use of other oxidants like Cu^{2+} [30] or ammonium persulfate [31]. These findings are particularly interesting and intriguing because the film deposition was performed in acidic conditions, in which no film deposition occurs when O_2 is used as an oxidant owing to kinetic limitations. In addition, the first step of the reaction cascade leading to polydopamine is the oxidation of dopamine to dopamine quinone with the loss of two protons and two electrons. This reaction is coupled with the reduction of oxygen, and the overall redox reaction is independent from pH from a thermodynamic point of view, but its kinetics is strongly pH dependent. Another interesting finding is that polydopamine films can also be produced by electropolymerization of deoxygenated dopamine solutions. In this case, the maximal film thickness reached from 2 g L^{-1} dopamine solutions is similar to that obtained when O_2 is the oxidant, nevertheless the permeability of both kinds of films for hexacyanoferrate anions is markedly different [32], suggesting that the electropolymerized films have a different porosity than those obtained in the presence of O_2.

The only way to have better insights into the reaction mechanism of film deposition is through a careful examination of the deposition kinetics of such films. The kinetics of polydopamine film deposition has been investigated by means of electrochemical quartz microbalance in the case of films obtained through electropolymerization [33], with Atomic Force Microscopy [1] and ATR-FTIR spectroscopy in the case of films made in the presence of an oxygenated dopamine solution [34] and by optical methods [29]. However, in these investigations, the concentration of dopamine was not varied. It is hence the main aim of this article to investigate the deposition of polydopamine films as a function of dopamine concentration in solution at a constant pH of 8.5 in the presence of Tris buffer which appears as "standard" conditions for the deposition of such films. We will focus on the film thickness as a function of time, on the surface energy of the coatings when the maximal thickness is reached, on the film morphology as a function of the dopamine concentration and time. We will also perform some impedance spectroscopy measurements as a function of the same parameters to investigate the evolution of the electrochemical impedance from the pristine electrode up to a surface fully covered with an amorphous organic coating. Finally, we will discuss our data in the framework of a kinetic model providing a rate equation able to fit the deposition kinetics in a satisfactory manner.

2. Materials and methods

All the solutions were prepared from Milli Q water (Millipore Simplicity system) having a resistivity of 18.2 MΩ cm. The solutions were buffered with 50 mM Tris(hydroxymethyl) aminomethane) (Ref. 252859, Sigma Aldrich) which will be called Tris buffer in the following. Its pH was adjusted from 10.1 with concentrated hydrochloric acid down to the desired value. This molecule was used as a buffer and supporting electrolyte even for pH values outside its buffering window lying between pH 7.2 and 9.2 to avoid specific buffer effects on the deposition of polydopamine films [30]. Dopamine hydrochloride was purchased from Sigma–Aldrich (Ref. H8502) and used without further purification. Dopamine was dissolved in Tris buffer just before the beginning of each deposition experiment. The solutions were vigorously agitated by means of magnetic stirring (300 rpm). Even if dopamine is highly soluble in water, at least up to 20 g L^{-1} at pH 8.5, we restrict our investigation to concentrations lower than 5 g L^{-1}, hence 26 mM in dopamine hydrochloride due to the limited solubility of oxygen in water, which is of about 10^{-3} mol L^{-1} at 25 °C. Even in these conditions, oxygen is the limited reactant and the solution needs to be under constant agitation in an open reactor to allow for a constant supply in oxygen All deposition experiments were performed in a similar sized beaker covered with a perforated aluminum foil to allow for contact with air and hence oxygen. The ratio of the solution's volume to the total surface of the absorbents (silicon wafers + walls of the beaker) was the same in all experiments. Evaporation losses were compensated regularly by the addition of Milli Q water. The substrates to be coated, silicon slides (P doped from Siltronics, Archamps, France, cut in rectangles of 4×1 cm^2 with a diamond knife) or working electrodes for electrochemical experiments, were glued on the walls of the beaker glass with double sided scotch tape. The polished face of the silicon slides was exposed to the dopamine containing solution. The silicon slides or the working electrode to be used in electrochemical experiments were removed from the solution after a given reaction time, rinsed with distilled water and blown dry under a slight stream of nitrogen. The coatings deposited on silicon slides were then characterized by either ellipsometry, atomic force microscopy (AFM) or contact angle goniometry. The coatings deposited on amorphous carbon working electrodes were used for characterization by electrochemical impedance spectroscopy (EIS).

The working electrode for cyclic voltammetry and impedance spectroscopy was an amorphous carbon disk 1 mm in diameter (CH Instruments Ref. 104). This electrode was polished before each deposition experiment first with SiC polishing paper, then with diamond paste containing 1 μm particles (Reflex TM) and finally with γ alumina powder containing 50 nm particles (Buehler, Lake Bluff, Illinois). The polished electrode was then submitted to sonication steps, each one lasting over 2 min, in the presence of Milli Q water. The quality of the electrode polishing was checked by means of cyclic voltammetry. The experiment was performed using a Gamry 600 potentiostat in a two electrode configuration using an Ag/AgCl electrode (Ref. CHI 111) as both the reference and counter electrode. The EIS spectra were acquired in the presence of 50 mM Tris buffer at pH 8.5 containing 150 mM NaCl as well as 1 mM potassium hexacyanoferrate (Sigma P9387) as the electroactive species. The DC potential was set at 0.25 V versus Ag/AgCl corresponding to the potential at which the maximal oxidation current was found on the pristine amorphous carbon electrode. The AC potential was of 5 mV, and its frequency was varied from 10^5 to 10^{-2} Hz with 12 acquisitions performed per frequency decade.

Cyclic voltammograms (CVs) were also acquired on the pristine and polydopamine coated electrodes. For these experiments, the potential versus Ag/AgCl was scanned in between −0.1 and 0.7 V and back to −0.1 V at a potential scan rate of 50 mV s^{-1}.

The film thickness was investigated by single wavelength ellipsometry (PZ 2000; Horiba, France) at an incidence angle of 70° and a wavelength of 632.8 nm (He–Ne laser). The polydopamine films were deposited on rectangular silicon wafers immediately after the cleaning procedure. This cleaning consisted in the successive immersion of the wafers in a 2% (v/v) Hellmanex solution (Hellma, GmbH, Germany) during half an hour, intensive rinse with Milli Q