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Polyelectrolytes to produce nanosized polydopamine

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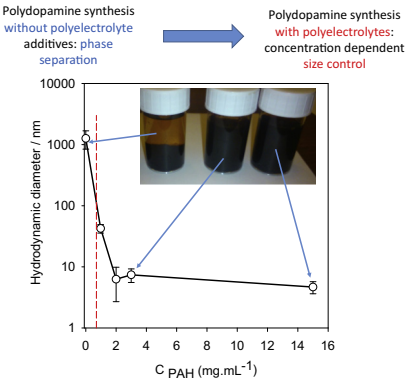
GRAPHICAL ABSTRACT



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ABSTRACT

"Polydopamine" (PDA) is the oxidation product of dopamine and can be obtained as thin films covering the surface of all kinds of known materials and simultaneously as insoluble and useless precipitates from dopamine solutions in the presence of appropriate oxidants. The valorization of such precipitates to obtain stable suspensions of functional nanomaterials is highly desirable owing to the chemical and optical properties of PDA. We show that a vast repertoire of polyelectrolytes polycations as well as polyanions, allow to control the size of PDA particles in the 10–100 nm size range. Simultaneously to the production of smaller nanoparticles, a progressive inhibition of PDA deposition on the surface of quartz plates (as well as on the surface of the reaction vessel) is found as the concentration of the polyelectrolytes is increased in the dopamine solution. The mechanism of size control-inhibition of film deposition is investigated in the particular case of poly(allylamine) but remains not understood in the case of polyanions.

1. Introduction

«Polydopamine» (PDA) films have emerged as a versatile surface functionalization method since such coatings can be deposited on the surface of all known materials [1,2] in a one pot reaction using dopamine or other catecholamines [3] as building blocks. Oxidants like water solubilized oxygen, Cu^{2+} cations [4] and other oxidants like periodate and peroxodisulfate anions [5] are used to oxidize the catecholamines and to allow for film deposition. The oxidation of dopamine is followed by its cyclisation to yield dopaminechrome, and finally 5,6-dihydroxyindole (DHI), the fundamental building block of eumelanins. DHI can then undergo aryl–aryl couplings at 4

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different positions (however with different reactivity) yielding many different isomers of dimers and later on many other oligomers of DHI, explaining the structural complexity and heterogeneity [6,7] of eumelanins, the natural photoprotectant of the skin [8]. Neuromelanins are made from the oxidation of dopamine whereas the black eumelanin from the skin is produced from L-tyrosine via enzymatically-triggered conversion to DOPAquinone [9].

Even if PDA films offer a plethora of applications in the field of water purification, energy conversion and as biomaterials [10,11], the fact that this eumelanine like material is not only produced on the surface of the material to be coated but also in solution has often been neglected. This comes mostly from the fact that the colloids obtained in solution are not stable with respect to colloidal aggregation and yield to progressive phase separation. The discovery that adjuvant like poly(vinyl alcohol) [12] and surfactants [13] or human serum albumin (HSA) [14] allow to considerably reduce the size of the eumelanin like aggregates, totally changed the perspectives on these eumelanin like colloids. In the case of surfactants, the deposition of PDA films on solid substrates was strongly inhibited from oxygenated dopamine solutions whereas the size of the particles in solution progressively decreased from a few μm in hydrodynamic diameter to a few nm when the concentration of surfactants (SDS and CTAB) was increased above their critical micellar concentration [13]. The size of the obtained PDA particles was found to be only slightly larger than the size of surfactant micelles, suggesting that the production of the eumelanin like material maybe favored in the surfactant micelles acting as a reaction template [13].

In the case of HSA, the obtained results suggest a similar mechanism [14]. However, HSA is only one particular protein being negatively charged at the pH = 8.5 at which the PDA nanoparticles were synthesized. Hence, it is of the highest interest to know if polyelectrolytes differing in the sign of their charge as well as in the nature of the charged group could play a similar role.

As a main result, it is found herein that many polyelectrolytes are effective in reducing the size and in inhibiting (in a concentration dependent manner) the deposition of PDA films. In the particular case of a polycation carrying primary amine groups, poly (allylamine hydrochloride), it will be shown that the presence of the amino groups on the polycation interferes with the self-assembly of PDA. In the case of a polyamine carrying quaternary amines, like poly(diallyldimethylammonium chloride), the mechanism by which the size of PDA is controlled is different, most probably with steric and electrostatic stabilization. Polyanions like poly (sodium-4-styrene sulfonate) and sodium polyacrylates exert a similar control in the size of PDA aggregates and inhibition of film deposition on solid surfaces but in a still unexplained manner since PDA is by itself negatively charged in the conditions of film deposition.

The possibility to produce stable PDA colloidal particles will offer new fundamental challenges to understand the structure of those particles and for applications in which a stable eumelanin like material is required. In this article we will call the obtained materials either X-PDA or PDA to compare the material obtained in the presence of the polyelectrolyte X and PDA obtained in the presence of Tris buffer in the presence of dissolved 0_2 acting as an oxidant.

2. Materials and methods

2.1. Chemicals, adsorption substrates and synthesis of PDA

All aqueous solutions were prepared from distilled and deionized water (Milli Q+, Millipore, ρ = 18.2 MΩ cm). The synthesis of PDA was performed at pH = 8.5 in the presence of Tris buffer (50 mM Tris(Hydroxymethyl)aminomethane, Prolabo France) from a 2 mg mL^{-1} dopamine solution (Sigma, Ref. H8502). The synthesis was performed either without polyelectrolytes or in the presence of polyelectrolytes at different concentrations. Dopamine was dissolved either in the Tris buffer or in the Tris buffer where the added polyelectrolyte was dissolved before dopamine addition. The dissolution of dopamine defined the time $t = 0$ of the reaction. The reaction medium was exposed to air and shaken at 300 rpm by magnetic stirring. Regularly some water was added to compensate for evaporation. The reaction was performed at (25 ± 5) °C. The temperature was regularly measured during the course of an experiment.

The polyelectrolytes used as adjuvents during the synthesis of PDA were poly(allylamine hydrochloride) (PAH, Ref. 283215, M_w = 15,000 g mol^{-1} as characterized by means of GPC using PEG as a standard), poly(diallyldimethylammonium chloride) (PDADMAC, Ref. 409022, molecular mass between 2×10^5 and 3.5×10^5 g mol^{-1}), poly(sodium styrene sulfonate) (PSS, Ref. 24,305-1, molecular mass $\sim 7 \times 10^4$ g mol^{-1}) and poly(acrylic acid) (PAA, Ref. 181285, molecular mass $\sim 4.5 \times 10^5$ g mol^{-1}). They were purchased from Sigma–Aldrich and used without further purification.

The PDA and X-PDA films were deposited on freshly cleaned quartz slides (Thuet, Blodelsheim, France) and on silicon wafers (Siltronix, Archamps, France). The slides were cleaned in a 2% (v/v) Hellmanex (Hellma Gmbh, Germany) solution at 60 °C during 30 min, rinsed with distilled water, immersed during 10 min in 0.1 M HCl, and finally rinsed with distilled water.

2.2. Characterization methods

The quartz or silicon slides were removed from the reaction medium after different oxidation times of dopamine, intensively rinsed with distilled water and blown dry with a stream of nitrogen. The absorption spectrum of the PDA films was recorded between 200 and 800 nm in wavelength with a double beam mc^2 spectrophotometer (Safas, Monaco, France) taking a cleaned quartz slide as the reference.

The silicon wafers were also removed from the reaction medium and the thickness of the pristine-PDA or X-PDA coatings was determined by means of single wavelength (λ = 632.8 nm) ellipsometry (PZ2000, Horiba, France). The PDA and X-PDA coatings were modelled as homogeneous and isotropic films having a refractive index of 1.73-0.02i at 632.8 nm as determined previously [15]. The obtained thickness values correspond to the average (± one standard deviation) over 5 measurements along the major axis of the rectangular silicon slides.

The hydrodynamic diameter of the colloids obtained in solution was measured by dynamic light scattering (Nano ZS, Mavern Instruments, λ = 632.8 nm, scattering angle: 173°) after 24 h of reaction. The intensity autocorrelation function was analyzed with the Contin algorithm and the results are plotted as the variation of the hydrodynamic diameter versus the concentration of the adjuvant (polyelectrolyte) added to the reaction mixture. The hydrodynamic diameter was calculated from the obtained diffusion coefficient using the Stokes–Einstein equation. The error bars given in the figures correspond to the width of the size distributions given by the software. The DLS experiments were performed without separation of X-PDA from the unbound polyelectrolytes.

2.3. NMR experiments

After lyophylization the X-PDA samples were packed in 4 mm rotor. The ^{13}C CP/MAS experiments spectra were recorded at 298 K on a Bruker Solid State DSX 300 MHz NMR spectrometer equipped with a Bruker 4 mn $^1H/X$ CP/MAS probe. A shaped Cross-Polarization pulse sequence with tangential modulation on