



Spontaneous deposition of polylysine on surfaces: Role of the secondary structure to optimize noncovalent coating strategies



Alessandro Di Mauro^a, Francesca Mirabella^b, Alessandro D'Urso^b, Rosalba Randazzo^b, Roberto Purrello^b, Maria Elena Fragalà^{a,*}

^a Dipartimento di Scienze Chimiche and INSTM Udr Università di Catania, Viale A. Doria, 6, 95100 Catania, Italy

^b Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria, 6, 95100 Catania, Italy

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ABSTRACT

Understanding the factors that governs spontaneous molecular transfer from solution to solid surface is fundamental to control noncovalent surface functionalization strategies, both in term of robustness and reproducibility. The comprehension of the nature of interaction involved in the mechanism of spontaneous adsorption will allow for a fine modulation of the deposition process. Herein, we provide experimental evidences to demonstrate that poly-lysine secondary structure represents a crucial factor profoundly influencing the outcome of its spontaneous deposition on quartz surfaces. In particular, random coil to α -helix transition is required to drive an effective transfer of the poly-L-lysine at the liquid–solid interface. β -sheet deposition requires longer times to be accomplished, while random-coil deposition is highly unfavored. Accordingly, polylysine deposition on quartz and silicon is effective when α -helix is formed in solution ($\text{pH} > 10$). This surface noncovalent functionalization represents a simple strategy to fabricate hybrid organic–inorganic or biocompatible materials. In fact, the proposed methodology is proven robust and repeatable and compatible for combination with solution or vapor phases (i.e. MOCVD) nanomaterial deposition approaches.

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1. Introduction

Poly-L-lysine (PLL) coated surfaces are conventionally used to promote cell adhesion or as cationic counterpart in the layer-by-layer deposition of ionic biopolymers and biomolecules [1,2]. PLL can assume three canonical conformations (α -helix, random coil and β -sheet) depending on pH and, in the case of β -sheet, temperature (Fig. S1, Supplementary Informations) [3]. In particular, pH values lower than ≈ 10 (i.e. in conditions in which amino groups in the side chains are protonated, being their $\text{pK}_a \approx 10$) lead to random coil conformations, which switch to α -helix at higher pH when the charge repulsion is partly released. Increasing the temperature, in the latter pH conditions, PLL adopts a β -sheet conformation.

Despite the richness of conformations (strictly related to charge exposition) the influence of the various secondary structure of PLL on spontaneous deposition effectiveness on solid surfaces has been largely overlooked, and the main focus was deserved to the mere electrostatics of the investigated systems (i.e. substrate and

overlayer) [4]. Then, most of the procedures used to deposit PLL on negative substrates (SiO_2) deals with polypeptide solutions at neutral pH; that is in conditions in which PLL is cationic (and in random coil conformation, owing to the protonation of the side chain amino groups) and the maximum electrostatic attractions with quartz should be reached. The idea of studying the role of conformations on the deposition history of PLL derives from a recent publication of our group [5]. We have found, in fact, that PLL deposition on quartz is optimized under unexpected process conditions ($\text{pH} \geq 10$). These results have been achieved by using the anionic meso-tetrakis (4-sulphonato phenyl) porphyrin ($\text{H}_2\text{-TPPS}$) as (indirect) probe of the efficiency of PLL deposition. According to simple electrostatics considerations, the tetra-anionic porphyrin does not adsorb indeed on quartz surfaces. Yet, deposition of PLL onto anionic quartz surface causes the reversal of the substrate surface charge thus allowing for subsequent loading of anionic H_2TPPS onto the PLL treated solid surface. Interestingly and unexpectedly, experimental findings pointed out that loading of H_2TPPS is more effective when PLL is deposited from basic ($\text{pH} \geq 10$), rather than neutral or acid solutions.

This result was largely unexpected since, according to electrostatic consideration, a stronger binding at neutral or acid pH was predicted in analogy with the behavior of similar systems, as, for

* Corresponding author.

E-mail address: me.fragala@unict.it (M.E. Fragalà).

instance, the formation of stable aggregates of DNA-cationic porphyrinoids [6] or polylysine with anionic porphyrins [7].

From these data, then, it turns out that the simple electrostatic model is not enough and other effects have to be considered to fully understand PLL deposition on quartz [4,5]. Circular dichroism (CD) represents a powerful techniques to follow, in solution, the conformational changes of polypeptides and other biological macromolecules induced by several environmental factors [8]. However, despite the crescent interest towards chiral materials [9] solid state CD is more complex [10] and the sensitivity of the technique is often not sufficient to study the conformational arrangement of molecular layers self-assembled on solid surface. Herein, we used the sensitivity of CD technique to test the outcome of spontaneous deposition of PLL on quartz, and we offer new insights on the effect of secondary structure to achieve a more robust, effective and ecofriendly (in water) deposition. The identification of the optimal parameters to spontaneously deposit, in water, silicon based substrates with PLL allow us to optimize noncovalent strategies to prepare functional materials. In particular, we demonstrate how water soluble tetra-substituted anionic porphyrins can be easily and efficiently deposited on ZnO layers grown by Metallorganic Chemical Vapor Deposition on quartz substrate [11], without using covalent functionalization steps [12,13]. The elevated extinction coefficient of porphyrin will allow for an immediate optical response of the deposition outcome as well as a rough quantification [5,13]. Another important application of PLL treated surfaces will be related to silver nanoparticles (AgNP) surface coating. Among the most used nanomaterials, AgNPs possess many useful optical, physical, and chemical properties. They are considered excellent antimicrobial agents [14] and plasmonic materials [15,16]. Spontaneous deposition of AgNPs colloidal solutions onto untreated quartz or silicon surfaces is difficult to be attained. In fact, citrate capped AgNPs are negatively charged at neutral pH and, accordingly, strongly repelled by silica and silicon. On the contrary, if the surface are treated with PLL, the positive charged beard at neutral pH promote nanoparticles adhesion, whose entity will mostly depend on pH regulation of PLL solution rather than deposition time.

2. Materials and methods

2.1. Solutions preparation

Poly-L-lysine hydrochloride (PLL, Dp 425) was purchased from Sigma Aldrich, as lysinated salt. Aqueous solutions were prepared using Millipore water. The concentration of the PLL solutions was measured spectrophotometrically (using $\epsilon_{205} = 3300 \text{ M}^{-1} \text{ cm}^{-1}$ in water). NaOH (6 M) or HCl (6 M) were used to adjust pH in the investigated range (from pH = 7 to pH = 10.5). The α -helix to β -sheet transition is promoted by heating the PLL solution at 60 °C for 1 h. Meso-tetrakis(4-sulfonatophenyl)porphyrin (H_2TPPS) was purchased from Midcentury as tetrasodium salt. Mother solutions of this porphyrin ($1.4 \times 10^{-4} \text{ M}$) were prepared in Millipore water. The concentration of diluted porphyrin solutions ($1 \mu\text{M}$) was measured spectrophotometrically using $\epsilon_{413} = 4.8 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ in water.

2.2. Surface modification

Quartz slides (Heliosquartz) were used after sonication in isopropyl alcohol (5 min), methanol (5 min) and water (5 min). After washing, quartz slides were dipped in PLL solutions having different concentration (from $1 \times 10^{-3} \text{ M}$ up to $25 \times 10^{-3} \text{ M}$) for a defined time (ranging from 30 min up to 24 h). CD analysis of the PLL functionalized quartz slides was performed after drying

in air. After, samples were washed with water and wipe-dried, before dipping in H_2TPPS ($1 \mu\text{M}$, pH = 7, 2 h).

2.3. ZnO deposition and surface functionalization

ZnO was deposited by Metal Organic Chemical Vapor Deposition (MOCVD) on washed quartz substrates. The deposition was performed in a hot wall tubular reactor, using as precursor a diamine (N,N,N',N'-tetramethylethylenediamine) (TMEDA) adduct of zinc(II) bis (2-thenoyl-trifluoroacetate), ($\text{Zn}(\text{tta})_2\text{tmEDA}$), Ar (250 sccm) and O_2 (250 sccm). The substrate temperature was 650 °C and the deposition time is 60 min. After deposition, samples were dipped in PLL aqueous solution (1 mM) at pH > 10, for 30 min. After washing in water to remove unbound PLL, the samples were dipped in H_2TPPS aqueous solution ($1 \mu\text{M}$) solution at pH = 7, for 2 h. After dipping, samples have been washed with water and wipe-dried.

2.4. AgNP citrate-capped synthesis

Silver nanoparticles was prepared by the modified method of Řezanka et al. [17]. Briefly, 0.5 mL of an aqueous solution of silver nitrate (1%) was mixed to an equivalent volume of an aqueous solution of sodium citrate (1%) and added to 50 mL of boiling ultra-pure water. The obtained solution was heated for 20 min and it turns from colorless to brown–yellow. After heating, the obtained solution was cooled down to room temperature and used after 1:1 dilution in water.

2.5. AgNP deposition on PLL treated surfaces

PLL treated (30 min, PLL 1 mM, pH = 10.5) quartz and silicon substrates were dipped in diluted (1:1) AgNP solution at different times (ranging from 5 min to 24 h). After dipping, samples were washed with water and wipe-dried.

2.6. Sample characterization

UV/Vis spectra were collected using a JASCO V-635 spectrophotometer using 1 cm pathlength quartz cells. The circular dichroism (CD) spectra were recorded on a JASCO J-810 spectropolarimeter, equipped with a 450 W xenon lamp. XPS analyses were performed using a PHI ESCA/SAM 5600 multi technique spectrometer equipped with a monochromatized Al K α X-ray source operating at 250 Watt and a base pressure of 10^{-10} mbar. Sample morphology was studied using a Field Emission LEO SUPRA scanning electron microscope (FE-SEM) equipped with energy dispersive X-ray spectroscopy (EDS, Oxford Instruments). X-ray Diffraction (XRD) was performed using a Bruker θ - 2θ diffractometer, using filtered Cu K α radiation.

3. Results and discussions

3.1. Optimization of PLL deposition on glass: an insight on the role of secondary structure

Inspired by the modeling of solvation dynamics of secondary structure of proteins [18] and from the partial lack of models concerning the transfer from solutions to solid surfaces [4] we assumed that molecular interactions of PLL polar side chains with an oppositely charged surface (quartz) should be strongly affected by conformational rearrangements. To confirm this assumption we used circular dichroism (CD) to correlate the outcome of PLL deposition on quartz to the assumed secondary structure (Fig. 1).

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