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Counterions in layer-by-layer films—Influence of the drying process

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Abstract

The amount of counterions, measured by means of X-ray photoelectron spectroscopy (XPS), in layer-by-layer (LbL) films of poly(allylamine hydrochloride) (PAH) and poly(styrene sulfonate) (PSS), prepared from solutions with various NaCl concentrations, is shown to be greatly influenced by the film drying process: a smaller amount of counterions is observed in films dried after adsorption of each layer, when compared with films that were never dried during the film preparation. This is attributed to the formation of NaCl nanocrystals during the drying process which dissolve when the film is again immersed in the next polyelectrolyte solution. The presence of bonded water molecules was confirmed in wet films indicating that the counterions near the ionic groups are immersed in a water network. The number of counterions is dependent on the amount of salt in polyelectrolyte solutions in such a way that for a concentration of 0.2 M the relative amount of counterions attains saturation for both dried and wet samples, indicating that the process which leads the aggregation of counterions near of the ionic groups is not influenced by the drying process. Moreover, it is proven for wet samples that the increase in salt concentration leads to a decrease in the number of PAH ionized groups as predicted by the Muthukumar theory [J. Chem. Phys. 120 (2004) 9343] accounting for the counterion condensation on flexible polyelectrolytes.
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1. Introduction

The layer-by-layer (LbL) technique has received significant attention over the last years mainly due to the possible large-scale fabrication of low cost molecular heterostructures for organic-based electronic and photonic devices [1–5] and sensors [6,7]. Since film formation is based on the alternate adsorption from aqueous solutions of oppositely charged polyelectrolytes onto solid substrates, it involves rather complex processes and phenomena that are still not fully understood. One of these phenomena concerns the presence of counterions in the LbL films as a result of complete or partial replacement of counterions by oppositely charged polyelectrolytes. Results in the literature are contradictory. In LbL films of poly(acrylic acid)/poly(allylamine hydrochloride) (PAA/PAH) [8] and poly(butanyl viologen) dibromide (PBV)/poly(styrene sulfonate) (PSS) [9] no counterions were found, in contrast to films of PSS/poly(diallyldimethylammonium chloride) (PDADMA) [10,11]. Although preliminary experiments failed to detect counterions [12] in films of PAH/PSS, the presence of counterions in those films has already been reported [13–15]. Recently, it was shown that counterions are incorporated in PAH/PSS LbL films with its amount tending to constant values as the ionic strength is increased [16]. The presence of counterions in these films was explained as a result of condensation of counterions and water molecules near polyelectrolyte ionic groups leading to an increase in the effective size of the polyelectrolyte ionic group and accounting for the increase in film thickness with ionic strength up to a constant value [16,17]. As a result, a region rich in counterions and water molecules is created between opposite polyelectrolyte ionic groups, like in an ionic network [16]. This is corroborated by the well-known presence of water molecules in LbL films [18–20] and by the thickness decrease when the samples are dried [18,21]. Although in 1994 Decher et al. [22] showed that the drying influences the film structure, there have been few studies of the drying effects. For example, Halthur et al. [23]

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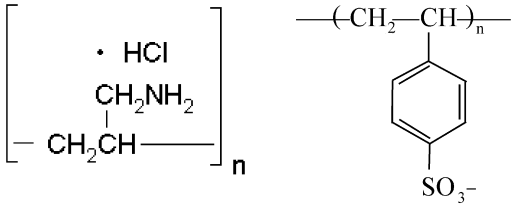
studied the stability of LbL films of poly(L-glutamic acid) (PGA) and poly(L-lysine) (PLL) taking into account the drying effect on thickness and refractive index and concluded that the intermediate drying and measurement in air does not affect the contribution for layer buildup. Moreover, upon drying the PGA/PLL LbL films thickness collapsed by as much as 70%, without any irreversible changes in the layer structure. Chen et al. [24] studied LbL films of diphenylamine-4-diazonium-formaldehyde resin (DR) and 2-nitro-*N*-methyl-4-diazonium-formaldehyde resin (NDR) and other polyelectrolytes and concluded that the samples dried after adsorption of each layer had higher adsorbed amounts than samples prepared without drying and showed that drying makes the films flatter and rather hydrophobic. It was also observed that drying at every step of adsorption increased the thickness of adsorbed films due to enhanced surface roughness of PAH/PSS LbL films [25]. De Souza et al. [26] noted that drying affects the film build-up and morphology, with LbL films dried under room conditions displaying a more homogeneous surface (lower roughness) and higher adsorbed amounts when compared with films dried under vacuum or by nitrogen flow. The lower roughness was attributed to lower solvent evaporation rates for samples dried in air. An increased ionic strength was also shown to lead to rougher surfaces [27]. Recently, Patel et al. [28] verified that the net growth of an enzyme layer increases when the drying step is omitted. Drying of enzymes layers reduces the activity of the assembly to some extent. With such conflicting evidence for the role of drying, one decided to investigate the effect from drying on the contents of counterions in PAH/PSS films LbL prepared from solutions having different ionic strengths. This article shows that the amount of counterions is influenced by the drying process and the presence of counterions in the LbL films changes the PAH degree of ionization.

2. Experimental

The LbL films were prepared from aqueous solutions of poly(allylamine hydrochloride) (PAH) (average $M_w = 50{,}000$–$65{,}000$ g/mol) and poly(styrene sulfonate) (PSS) ($M_w = 70{,}000$ g/mol) with concentrations of 10^{-2} M and with different sodium chloride concentrations. The polyelectrolyte concentrations were based on the molecular weight of the repeat unit. The chemicals, purchased from Aldrich, have their monomer structures shown in Fig. 1.



(a) PAH (b) PSS

Fig. 1. Polyelectrolyte molecular structures: (a) poly(allylamine hydrochloride) (PAH), (b) poly(styrene sulfonate) (PSS).

Pure water with a resistivity of 18 MΩ cm, supplied by a Millipore system (Milli-Q, Millipore GmbH), was used to prepare all aqueous solutions. For XPS measurements, 8-bilayer LbL films ($(PAH/PSS)_8$) were adsorbed onto 10×20 mm^2 substrates obtained from aluminum foils. The adsorption time for each layer was 10 min. The substrates were washed with pure water and dried with a nitrogen flow. In order to maintain the PAH electrically charged, solutions were obtained from pure water resulting in a pH of about 5. The films were prepared by washing the film with pure water after adsorption of each layer. Some samples were dried leaving the samples at room conditions after each layer adsorption for a few minutes (dried samples) and other samples were not dried between the adsorption of each layer (wet samples). Drying at room conditions was chosen in face of the results obtained by de Souza et al. [26], who reported more homogeneous surfaces and higher adsorbed amounts in LbL films dried at room conditions comparatively to those dried with a nitrogen flux.

To investigate the presence of counterions the samples were analyzed in an X-ray photoelectron spectrometer XSAM800 (Kratos) operating in the fixed analyzer transmission (FAT) mode [29], with a pass energy of 10 eV, a power of 130 W and the non-monochromatized Mg$K\alpha$ X-ray ($h\nu = 1253.7$ eV). All the samples were analyzed on the central part of the sample, i.e., over a 1×3 mm^2 spot area at an angle of 0° relative to the normal to the sample surface using the High Magnification mode. At least 2 specimens were analyzed for each preparation condition. The spectra were recorded with a Sun SPARC Station 4 with Vision software (Kratos) using a step of 0.1 eV. The X-ray source satellites were subtracted, Shirley background and pseudo-Voigt profiles (Gaussian and Lorentzian products) were fitted to each region using a non-linear least-squares algorithm. No charge compensation (flood-gun) was used. Binding energies (BE) were corrected by using aliphatic C 1s BE equal to 285.0 eV [30]. For quantification purposes, sensitivity factors were 0.66 for O 1s, 0.25 for C 1s, 0.42 for N 1s, 0.54 for S 2p, 2.3 for Na 1s, 0.73 for Cl 2p and 0.21 for Al 2s as described elsewhere [16]. As a remark, it is worth to mention here that the main source of error in quantification of a given XPS spectrum comes from the baseline definition. This error depends on the number of counts in the peak, N (relative error $\approx 1/\sqrt{N}$) and is displayed in all figures as error bars.

The UV–visible absorbance spectra of dried and wet $(PAH/PSS)_8$ LbL films prepared onto hydrophilized BK7 optical glass substrates were measured using a Shimadzu UV-2101PC spectrophotometer.

3. Results and discussion

3.1. Dependence of counterions with salt concentration

The XPS spectra revealed the presence of carbon (C), sulfur (S), oxygen (O), nitrogen (N), sodium (Na) and chloride (Cl) and allowed the evaluation of atomic percentages. In this work, square brackets with the element symbol in between refer to the calculated atomic percentage. The values obtained for wet samples, for different salt concentrations, have already been

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