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# Input from XPS for the characterization of thin films based on polyelectrolytes and proteins

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Immobilizing and controlling the behavior of proteins at interfaces is a key for the development of biofunctionalized materials for applications in medicine, diagnostic, biocatalysis, separation technologies etc. Polyelectrolytes are polymers that bear positive or negative charges, and that can be very useful to build protein-based biointerfaces. On the one hand, they can enter in the composition of polymer brushes for the controlled and stimuli-responsive adsorption of proteins, and on the other hand, they can be combined with proteins into multilayered thin films, using the layer-by-layer (LbL) assembly method. In this presentation, both aspects will be illustrated, and the contribution of XPS to the characterization and understanding of such systems will be highlighted.

Brushes of poly(ethylene oxide) (PEO) are known to prevent protein adsorption. Brushes of poly(acrylic acid) (PAA), a weak polyelectrolyte, are able to swell or shrink according to the pH and the ionic strength (I) of the solution. Using an appropriate combination of these two parameters, mixed PEO/PAA brushes are expected to either repel the proteins, or allow their immobilization. This was exploited first for the design of surfaces featuring reversible protein adsorption [1], then for the selective adsorption of a protein from a mixture [2]. Here, XPS was used: (i) to unravel the composition of the PEO/PAA layers, and computing the fraction of each polymer; (ii) to determine the thickness of the brushes; (iii) to monitor protein adsorption and desorption.

An innovative method for the incorporation of proteins in LbL coatings was designed, based on the complexation of the protein with a polyelectrolyte prior to the assembly of such protein-polyelectrolyte complex (PPC) with a polyelectrolyte of opposite charge [3,4]. This results in thin films made of three different compounds (one protein, two polyelectrolytes). XPS was used, among other analytical tools, to unravel the composition of the films. Therefore, markers were used related to each compound, and in a more sophisticated approach, the peak envelope of each compound was used for the spectral decomposition of the peaks recorded on the coatings.

Altogether, the full exploitation of the XPS spectra, and especially of the carbon peak, is shown to contribute to the characterization of protein- and polyelectrolyte-based biointerfaces.

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