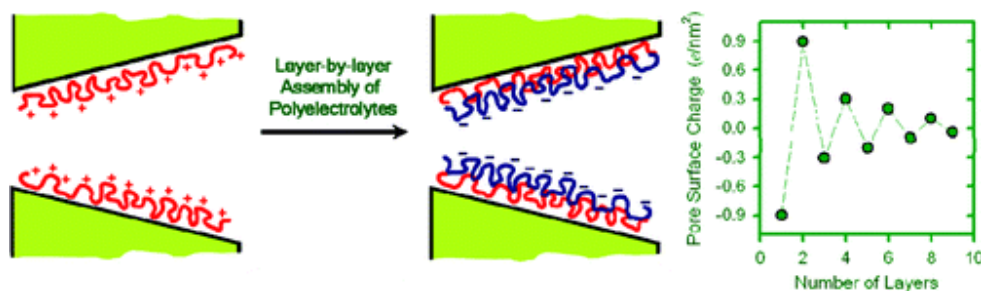


Layer-by-Layer Assembly of Polyelectrolytes into Ionic Current Rectifying Solid-State Nanopores: Insights from Theory and Experiment

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Molecular design of ionic current rectifiers created on the basis of single conical nanopores is receiving increasing attention by the scientific community. Part of the appeal of this topic relies on the interest in sensors and fluidic nanoactuators based on the transport of ions and molecules through nanopore architectures that can readily be integrated into functional systems. The chemical modification of the pore walls controls not only the diameter of these nanoarchitectures but also their selectivity and transport properties. In order to confer selectivity to solid-state nanopores, it is necessary to develop and explore new methods for functionalizing the pore walls. Hence, the creation of functional nanopores capable of acting as selective ion channels or smart nanofluidic sensors depends critically on our ability to assemble and build up molecular architectures in a predictable manner within confined geometries with dimensions comparable to the size of the building blocks themselves. In this context, layer-by-layer deposition of polyelectrolytes offers a straightforward process for creating nanoscopic supramolecular assemblies displaying a wide variety of functional features. In this work, we describe for the first time the integration of layer-by-layer polyelectrolyte assemblies into single conical nanopores in order to study and explore the functional features arising from the creation of charged supramolecular assemblies within the constrained geometry of the nanofluidic device. To address this challenging topic, we used a combined experimental and theoretical approach to elucidate and quantify the electrostatic changes taking place inside the nanopore during the supramolecular assembly process. The multilayered films were built up through consecutive layer-by-layer adsorption of poly(allylamine hydrochloride) (PAH) and poly(styrenesulfonate) (PSS) on the pore surface. Our results show that the charge transport properties of single conical nanopores functionalized with PAH/PSS assemblies are highly dependent on the number of layers assembled on the pore wall. In contrast to what happens with PAH/PSS films deposited on planar surfaces (quantitative charge reversal), the surface charge of the pore walls decreases dramatically with the number of PAH/PSS layers assembled into the nanopore. This behavior was attributed to the nanoconfinement-induced structural reorganization of the polyelectrolyte layers, leading to the efficient formation of ion pairs and promoting a marked decrease in the net fixed charges on the nanopore walls. We consider that these results are of paramount relevance for the modification of nanopores, nanopipets, and nanoelectrodes using charged supramolecular assemblies, as well as of importance in “soft nanotechnology” provided that structural complexity, induced by nanoconfinement, can define the functional properties of self-assembled polymeric nanostructures.