NANOCONFINED POLYELECTROLYTE BRUSHES: THERMODYNAMICS, ELECTROSTATICS AND TRANSPORT

Polyelectrolyte (PE) grafting on the solid-liquid interface of a nano-channel renders tremendous functionalities to the nano-channel. These grafted PE molecules attain "brush"-like configuration for large grafting density (σ), which makes the nano-channel (often denoted as *soft nano-channel*) capable of applications such as ion manipulation, ion sensing, current rectification, nano-fluidic diode action, and flow regulation.

The present thesis focuses on the theoretical modeling of the thermodynamics, electrostatics and transport of such nano-confined PE brush systems. The thesis starts by developing new scaling laws to a) determine the phase space for the grafting density (σ) and the polymer size or number of monomers (N_p) of the grafted PE molecules that ensure that the PE chains can simultaneously adopt a "brush"-like configuration and do not exceed the nano-channel half height, and b) identify the regime where the elastic and the excluded volume effects of the chains can be decoupled from the electrostatic effects. The subsequent part of the thesis is divided into two broad parts. In the first part, the thermodynamics, electrostatics, and the transport of PE-brush-grafted nano-channels in the *decoupled regime* is probed. In the second part, however, the analysis is carried out to elucidate the physical picture of the PE-brush-grafted nano-channels in the *coupled regime*.

For the analysis in the *decoupled regime*, firstly the electrostatics of such PE-brush-grafted nanochannels has been probed. These PE brushes are considered to exhibit pH-dependent charge density. The salient feature of the modeling is to account for the explicit hydrogen ion concentration in the corresponding electrostatics of the electric double layer (EDL) induced at the PE-brush-electrolyte interface. Results indicate profound influences of the hydrogen ion concentration, ionization constant of the PE brushes, salt concentration, and degree of confinement introduced by the nano-channel height in the overall electrostatics of the PE brushes.

Secondly, continuum-based modeling is conducted to study the transport in such pH-responsive PE-brush-grafted nano-channels by quantifying the corresponding electric-field-driven electroosmotic (EOS) transport and the ionic current in the decoupled regime. Results reveal highly dominant ionic current and tremendously suppressed electroosmotic transport – both these findings are massively significant in designing of highly efficient and programmable soft nano-channels for sensing ions and analytes.

The last part of the thesis is focused in studying the nano-confined PE brushes in the *coupled regime*, i.e., where the elastic and the excluded volume effects interplay with the electrostatic effects to determine the overall brush behavior.

Firstly, mean field theory models are developed to probe the electrostatics and configuration of PE brushes grafting the nano-channel inner walls. Results indicate highly non-intuitive swelling-shrinking behavior of end-charged brush, while for backbone-charged brush, one can always witness swelling behavior due to the electrostatic effect. Detailed free energy analysis is subsequently invoked in order to explain these non-trivial results for the end-charged brushes.

Secondly, ionic current and EOS transport in these end/backbone-charged-PE-brush-grafted nano-channels, with the brushes being described in the *coupled regime*, has been probed. Results indicate a most remarkable *enhancement* in the strength of the EOS transport. It completely reverses the standard understanding that the EOS transport is invariably suppressed in PE-brush-grafted nano-channels owing to the additional drag introduced by the brushes. Finally, we further quantify how the salt concentration and pH values of electrolyte effects the ionic and EOS transport in nano-channels grafted with end/backbone-charged brushes.

We anticipate that the findings of the present thesis will provide completely new perspectives in understanding several unknown facets of PE-grafted nano-channels. These facets will be pivotal in not only designing soft nano-channels with novel functionalities that can potentially be applied in several disciplines ranging from nanotechnology to biomedical and biochemical engineering, but will also provide important clues to decipher the behavior of a myriad of biological and chemical systems (e.g., PE-grafted nanoparticles, sheathed bacteria, phage viruses, etc.) that bear certain geometric and physical resemblances to the PE-grafted nano-channel system.