ABSTRACT

Title of dissertation: ENHANCED DIFFUSIOOSMOSIS AND THERMOOSMOSIS IN POLYELECTROLYTE-BRUSH-FUNCTIONALIZED NANOCHANNELS

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One of the holy grails of nanofluidic systems, which have attracted massive attention over the last couple of decades for applications in a plethora of disciplines ranging from bioengineering and energy to health and security, is to ensure a significantly large volume flow rate without the application of too large a pressure gradient. This has motivated the researchers to study different mechanisms of liquid transport in nanochannels involving physical effects that exploit the significantly large surface-to-volume ratio of such nanochannels. Some such examples include (a) electroosmotic transport triggered in presence of an external electric field, (b) surface-tension-mediated capillary-driven flow, etc. Very often such flows depend on surface treatment/functionalization of the nanochannel walls. For example, electroosmtic flow requires surface treatment to ensure that the nanochannel walls acquire surface charge. Similarly, capillary flows are better sustained in nanochannels whose walls are treated to acquire a large hydrophilicity. This thesis will focus on two particular non-pressure-driven but highly efficient flow mechanisms in such nanochannels that have

been functionalized by grafting the inner walls of the nanochannels by end-charged polyelectrolyte (PE) brushes.

Functionalization of nanochannels with PE brushes have seen massive interests and have been extensively used for a large number of applications ranging from ion manipulation, ion sensing, and biosensing to current rectification and fabrication of nanofluidic diodes. All these applications are solely dependent on the ion transport in the brush-functionalized nanochannels in the presence of an applied field and are benefitted by the fact that the electric field induced flow is significantly suppressed owing to the large drag force imparted by the brushes. In fact, this has been the well-accepted notion that the flows are invariably retarded in brush-grafted nanochannels: this is the reason that there are significantly less number of studies probing the flow phenomenon in brush-grafted nanochannels.

Very recently Das and Chen [1] established a completely new paradigm of electroosmotic (EOS) transport in nanochannels grafted with end-charged PE brushes. They established that such end-charged brushes localized the electric double layer (or EDL) charge density away from the nanochannel walls, which in turn ensured that the EOS body force triggered by the applied axial electric field is substantially away from the location of the maximum drag force that is near the nanochannel wall. As a consequence, the impact of the EOS body is severely enhanced leading to a substantial augmentation of the EOS flow strength. Of course, such augmentation greatly depends on the grafting density or the "looseness" of the grafting of the PE brushes. The enhancement is only witnessed if the brushes are sufficiently loosely grafted; for denser grafting, the drag force imparted by the brushes overwhelms the augmented influence of the localized EOS body force thereby leading to a significant retardation of the EOS flow.

In this thesis, such flow augmentation principle of nanochannel grafted with end-charged PE brushes is utilized to investigate two different nanocfluidic flow mechanisms. We first study an ionic difusioosmotic (IDO) transport in such end-charged brush-grafted nanochannels. IDO refers to a flow mechanism triggered by the application an external axial concentration gradient: this gradient induces (a) an electric field that drives an EOS transport and (b) a pressure-gradient dictated by the different in the diffusivities of the ions triggering a chemioosmotic (COS) flow. The study carefully points out (a) this induced electric field, (b) the overall DO transport and (c) the individual contributions of the EOS and COS flow fields in the overall DO transport. Our results unravel that the DOS transport is massively enhanced in nanochannels grafted with PE brushes with weak grafting density stemming from the signicantly enhanced EOS transport caused by the localization of the EOS body force away from the nanochannel walls. This augmentation is even stronger for cases where the COS transport aids the EOS transport. On the other hand, the DOS transport gets severely reduced in nanochannels grafted with dense PE brushes owing to the severity of the brush-induced additional drag force.

Secondly, we study an ionic thermoosmotic transport (ITO) in such end-charged brush-grafted nanochannels. ITO refers to a flow mechanism triggered by the application an external axial temperature gradient. The issues that are important here include: (a) the induced electric field and (b) the overall TO transport dictated by the induced-electric-field EOS transport, COS transport caused by the diffusivity difference of the EDL ions and a thermophoretic (TPT) transport caused by the difference in the preferential transport of the ions following the imposed temperature gradient. Here too the overall ITO is significantly enhanced as compared to the case of the brush-free nanochannels and we pinpoint the relative influence of the EOS, DOS, and the TPT transport in the overall ITO transport.

In summary, the present thesis provides a unique window on two possible flow mechanisms by which one can achieve a highly non-intuitive scenario where the flow in nanochannels can be significantly augmented by grafting the nanochannels with PE brushes. Given the universal difficulty in attaining a desirable flow strength in nanochannels, we anticipate that this thesis will serve as an important milestone in the general area of nanofluidics.