Active Nanopores 321821 Final Report (2012-2016)

Note the project website at: http://www.adahlin.com/ This is the webpage of the principal investigator. Several other funding sources have contributed to the project, as shown by the additional logotypes.

The project was dedicated to the development of novel types of solid state nanopores functionalized with polymer "brushes", i.e. dense layers of macromolecules that have one end grafted to the solid surface. The nanopores were characterized in structure and also in terms of their special optical properties, which are due to excitation of surface plasmons. The surface plasmons, in turn, offered a way to perform label-free real-time optical analysis of molecular binding to the surface and reactions inside the nanopores. The electrical control enabled by the continuous metal films in the structure also offered the possibility to change temperature and pH locally at the surface.

Some fundamental questions related to the behavior of macromolecules confined in limited space were addressed. For instance, the influence from negative curvature on the thickness of a polymer brush was investigated. The phase transitions of responsive polymer brushes inside nanopores were also investigated. This was done after developing and characterizing the same polymer brushes on planar surfaces. In terms of applications, the project evaluated the use of the polymer-functionalized nanopores for biomolecular filtration and entrapment. It was verified that proteins could not penetrate polymer brushes covering the nanopores and that responsive polymers made it possible to alter the permeability of the nanopores.

A list of the main achievements accomplished and published (at least in submitted manuscript form) during the timeline of the project is given here:

- We have developed new types of solid state nanopores that penetrate multilayers of thin gold films with insulators in between (publication in Adv.Opt.Mater. 2014). The optical properties were quantitatively described by a new theoretical framework based on surface plasmons in an arbitrary thin film multilayer (publication in J.Phys.Chem.C 2014). We also developed protocols to control nanopore diameter (publication in Analyst 2016). (Illustrated in Fig. 1.)
- Location-specific detection (publication in Nanoscale 2015). As a peripheral finding, which still has some relevance for the project, we found out that by monitoring several spectral features it is possible to use plamonic sensing to deduce where in the nanostructure binding occurs. This should be helpful when trying to understand the morphology of the polymer brushes inside the pores.
- Poly(ethylene glycol) brushes (publication in ACS App.Mater.Inter. 2015). We have presented a new strategy for creating thick and highly protein repellant polymer brushes by grafting the polymer to the surface. Since the molecular weight of the polymer is then characterized beforehand the brushes are very well defined. (Illustrated in Fig. 2.)
- Poly(N-isopropylacrylamide) brushes (publication under review in Appl.Surf.Sci.). By using atom transfer radical polymerization we managed to grow thermos-responsive polymer brushes on gold. We characterized the thickness of these brushes by a new methodology based on surface plasmon resonance. We also quantified how much the polymer brush could swell and contract upon changes in temperature. (Illustrated in Fig. 3.)
- Polypyrrole films (publication accepted in Adv.Mater.). We characterized the response from electrochemically grown polypyrrole films on the plasmonic nanopores. Although our initial study focused on the electrochromism of the hybrid material, these films should be useful also for controlling the permeability of the nanopores.

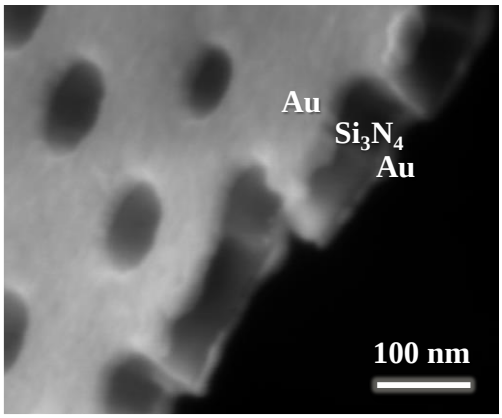

Figure 1. The most advanced nanopores fabricated in the project, with 100 nm pores penetrating three thin films of gold, silicon nitride and gold.

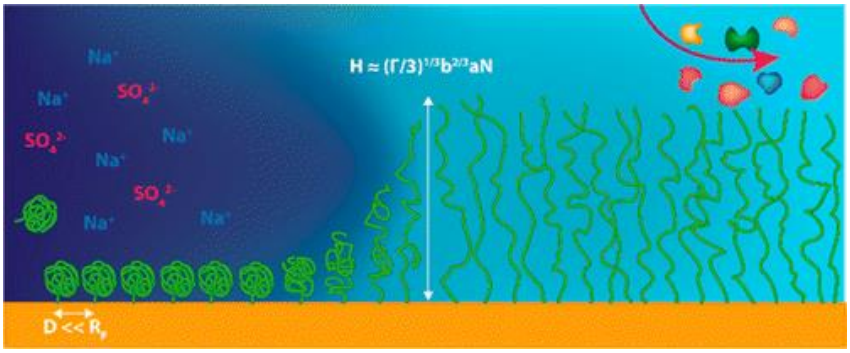

Figure 2. Principle schematic of grafting and protein resistance of poly(ethylene glycol) brushes. The images is the table of content graphic for the publication in ACS Applied Materials and Interfaces 2015.

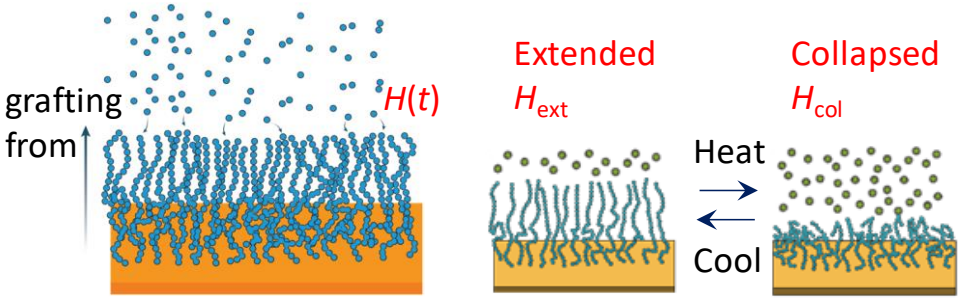

Figure 3. Principle schematic of growth and switching of thermo-responsive poly(N-isopropylacrylamide) brushes.

The project also generated interesting findings on the use of polymer-functionalized nanopores for biomolecular filtration and entrapment. These results are yet to appear in publications. In brief, we have shown that a polymer brush on the nanopores can act as a barrier with respect to proteins. Further, we have shown that it is possible to alter the permeability of the nanopores by resistive heating if they are functionalized with a thermo-responsive polymer brush.

The future impact of the research lies within lab-on-a-chip technologies (miniaturized analytical methods) and biosensor development. The functional nanopores can become an integrated part of microscale total analysis systems and increase the specificity in biosensors.