

# Biochemistry in Nano-Channels

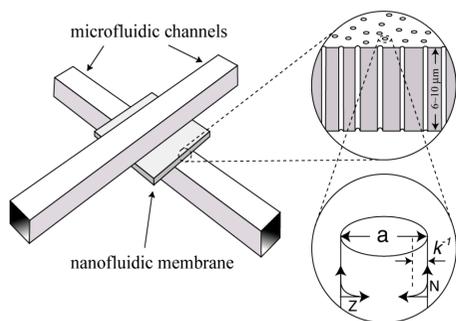
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## Goals

- To manipulate electrokinetic transport of molecules through nanocapillary arrays (NCA) in hybrid PMMA nano/microfluidic devices for chemical and biochemical applications.
- To construct multiple membrane stacks for better understanding of fundamental nanofluidics and molecular transportation properties.
- To enhance separation and characterization capabilities.
- To design all-silicon nano/microfluidic devices for reliable collection and separation of cell-to-cell signaling molecules.



*Far left.* Schematic diagram of the hybrid nano/microfluidic device with a nanocapillary membrane sandwiched between two microfluidic channels.

*Upper inset.* The cross-sectional schematic of the nanoporous membrane.

*Lower inset.* Schematic diagram showing relative sizes of the channel diameter ( $a$ ) and Debye length ( $\kappa^{-1}$ ) typically encountered with nanometer diameter channels and millimolar electrolyte solutions.  $Z$  is the distance from the nanochannel wall, and  $N$  is the ion number density.

## Mapping to Center's Objectives

- Create devices with selective transport, molecular recognition and concentration capabilities so that desired molecules can be fabricated and delivered as needed within the devices.
- Understand the transport and reaction mechanisms within the restricted space of the nanopore.
- Interface the output of these devices to powerful off-line chemical characterization approaches such as mass spectrometry.

## Fundamental Questions/Challenges

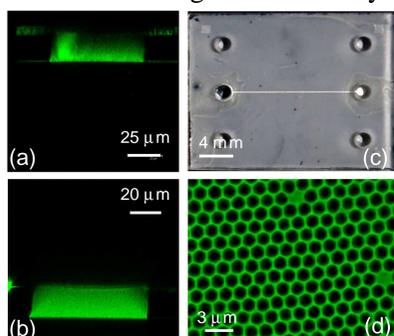
- Fabricate the inner nanopores in an NCA or a silicon with molecular recognition elements, thus creating the ability to transform molecules as they traverse the nanopores.
- Control the electrokinetic flow precisely for delivering sample plugs for separation and ultrafiltration.
- Enable fluidic manipulations and selective reactions within a multilayer device, including the deposition of analytes into nanopores and electrokinetic delivery of analytes to required locations.
- Characterize these efforts via mass spectrometry to validate the analyte transport.

## Research Plan

- Investigate the electrokinetic transport properties of the packed nano/microfluidic devices.
- Fabricate complex ultrafiltration devices with multiple membranes and multiple microfluidic channel layers.
- Develop multi-layer silicon microfluidic devices with nanoporous silicon membranes between layers.
- Test reliability of the silicon devices for long term applications.
- Create unique methods based on analyte adsorption to quantify compounds with mass spectrometry.

## Research Results

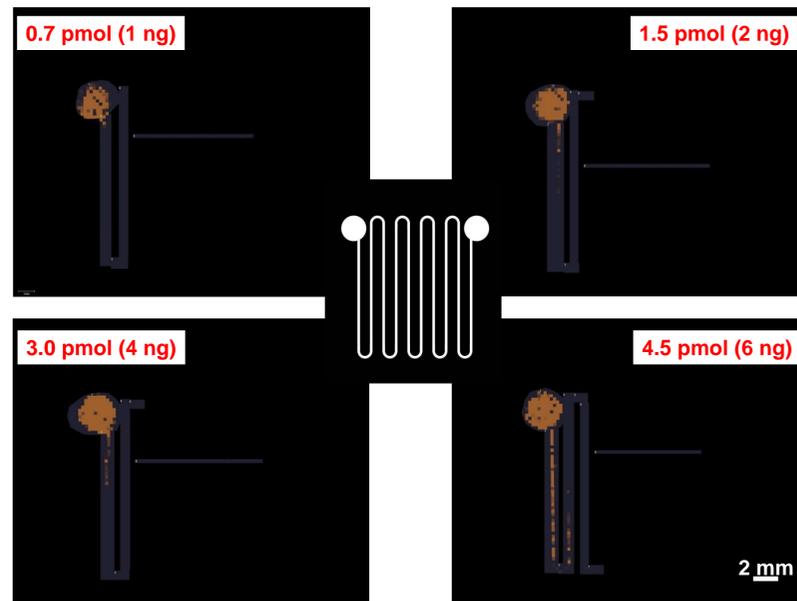
- Confocal images show ability to selectively pack a channel.



(a) Cross-sectional view ( $20 \mu\text{m} \times 80 \mu\text{m}$ ) of a packed channel produced with a packing angle of  $\alpha=20^\circ$ . (b) Cross-sectional view ( $20 \mu\text{m} \times 80 \mu\text{m}$ ) of a packed channel obtained with the channel at horizontal level. (c) Photograph of a microchip with a packed channel. (d) Confocal image of packed microbeads. Confocal images (a, b, and d) were obtained by filling channels with  $50 \mu\text{M}$  of FL solution; bare silica microbeads have uniform diameter of  $1.54 \mu\text{m}$ .

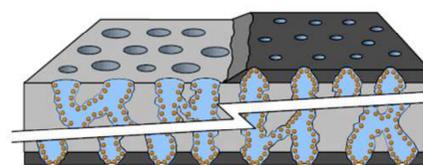
## Research Results (cont'd)

- Validation of mass-spectrometry-based quantitation in the device.

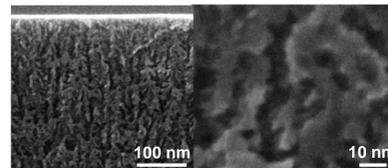


Mass spectrometric images of the collection channel with 0.7, 1.5, 3.0, 4.5 pmol Substance P (1347.7 Da, standard peptide) on a microfluidic device with a serpentine microchannel ( $110 \text{ mm length} \times 200 \mu\text{m width} \times 10 \mu\text{m height}$ ). A larger amount of peptide covers a longer portion of the channel; the length of channel that contains peptide can be related to peptide levels.

- Fabrication of nanoporous silicon membrane.



Schematic of the silicon porous membrane (light gray) with functionalized pore wall (orange) and thin layers of porous silica (dark gray) on both sides. Water (cyan) meniscus is stable even at low humidity ( $\sim 10\%$ ).



Cross section views of fabricated silicon membranes with uniform pore size. (Moghaddam and Shannon et al., Nature Nanotechnology, accepted)

## Broader Impact

- Centrifugal sedimentation provides a method for selectively packing microfluidic channels for improved separation capability based on LC-like mechanisms.
- Hybrid nano/microfluidic devices have unique properties for flow control and molecular transport.
- The layer-by-layer procedure for chip fabrication offers further integration of nano/microfluidic channels.

## Interaction with Other Projects

- Aluru*: Evaluation of molecular dynamics models of nanofluidic transport.
- Adesida/Ferreira*: Development and use of nanoporous materials for the deposition of a predefined pattern and fabrication of nozzle structure at the  $\text{SiN}_x$ .
- Shannon/Kenis*: Fabrication and characterization of hybrid PMMA/PCTE (or gold coated PETE) architectures; adoption of the new device made of silicon membranes for selective chemical transport and separation.
- Bohn*: Selective reaction and transport through nanopores.

## Future Efforts

- Integrate the porous silicon membrane with multilayer silicon microchannels for reliable capillary electrophoretic analysis.
- Develop approaches to follow the deposition process in nanofluidic channels that provides the requisite spatial, temporal and chemical information.
- Interface these devices to off-line chemical characterization efforts such as mass spectrometry.
- Apply the nano/microfluidic devices to selectively sample, modify and quantify complex samples.