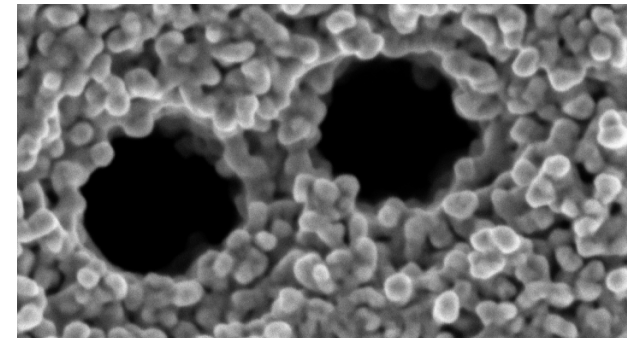
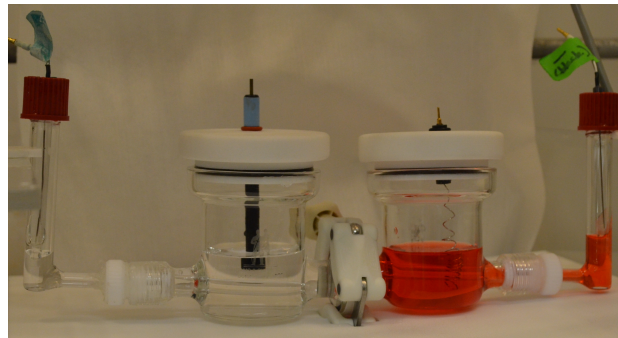
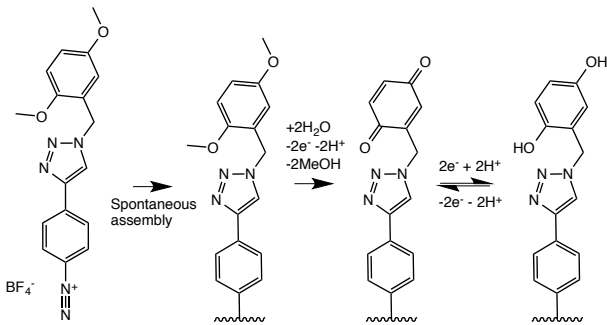


*Exceptional service in the national interest*

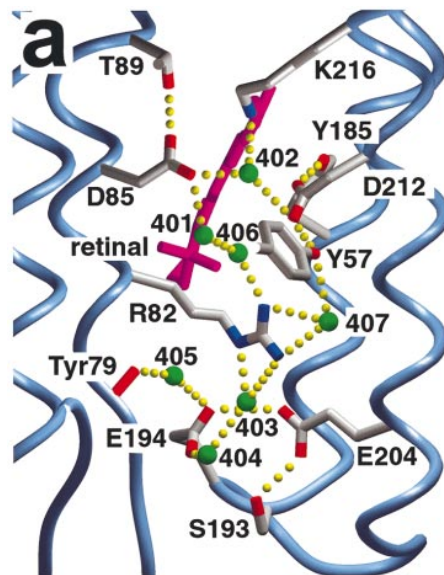


# Ion-Selective Nanoporous Polymer Membranes with Controllable Geometries and Switchable Surface Charges

Leo Small, David Wheeler, Erik Spoerke

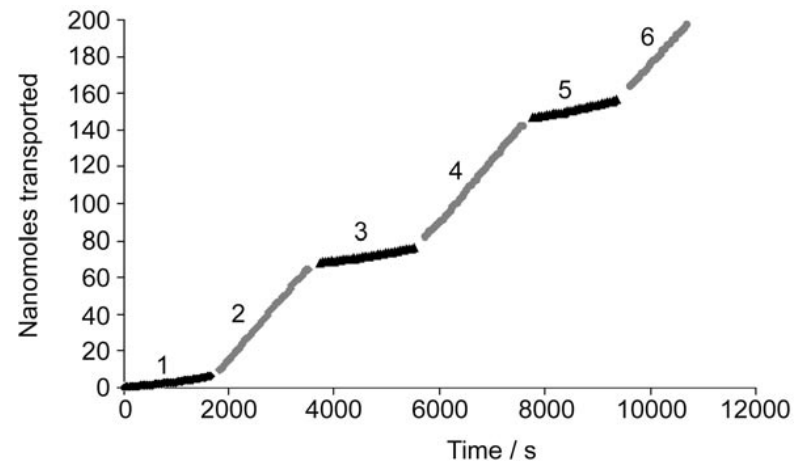
# Controlling Molecular Transport

- Mimic biological systems
- Regulate ionic gradients
- Switch via voltage, stable for long times



Structure of light-drive proton pump bacteriorhodopsin

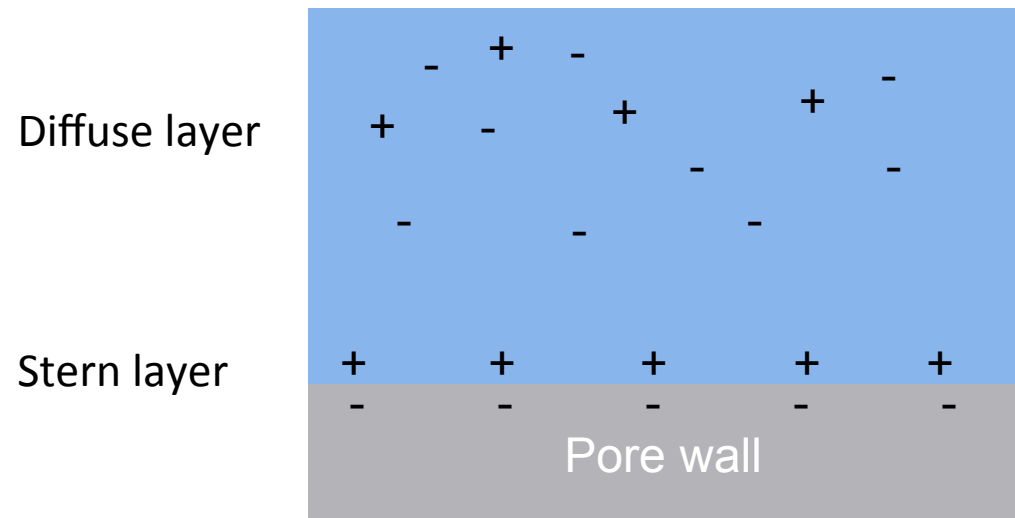
Luecke et al. *J. Mol. Biol.* **291** (1999) 899-911.



Voltage controlled transport of paraquat through a nanopore. Buyukserin et al. *Small.* **3** (2007) 266-270.

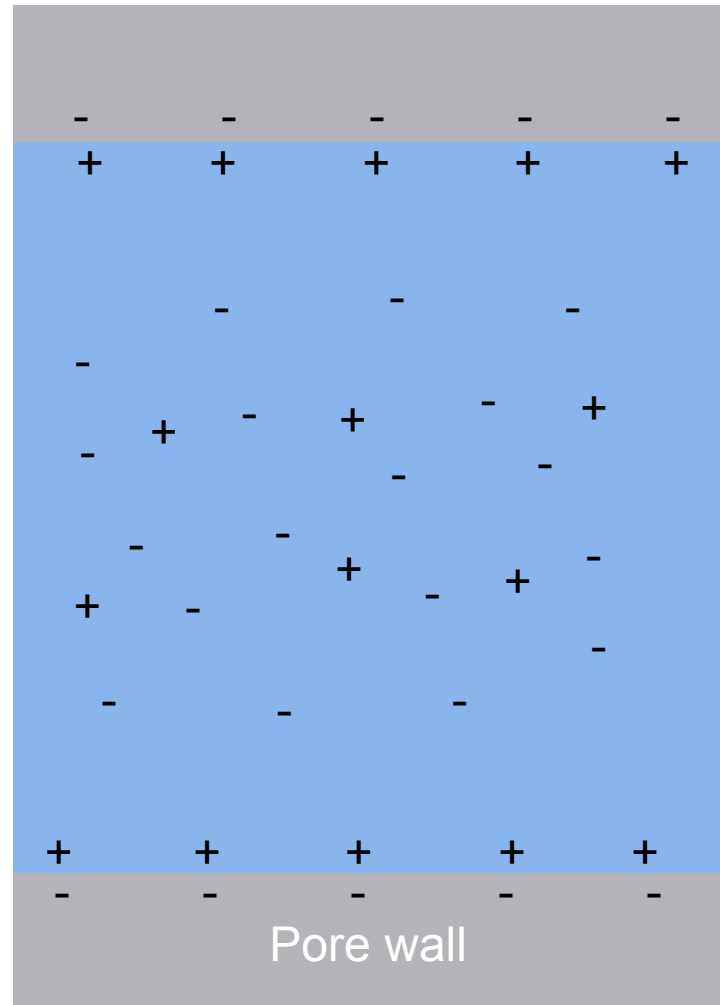
# Ion-Selectivity in Nanopores

- Controlling factors – solid-liquid interface



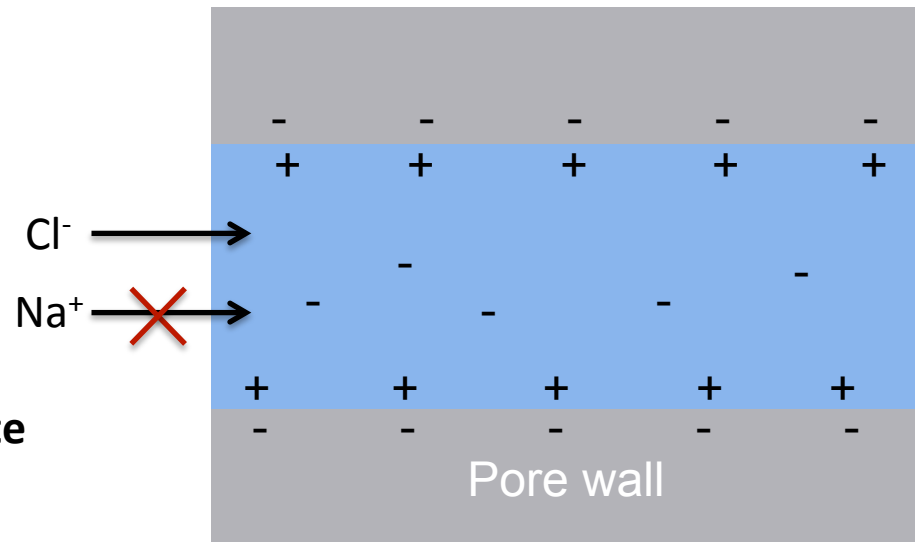
# Ion-Selectivity in Nanopores

- Controlling factors
  - Pore diameter



# Ion-Selectivity in Nanopores

- Controlling factors
  - Pore diameter

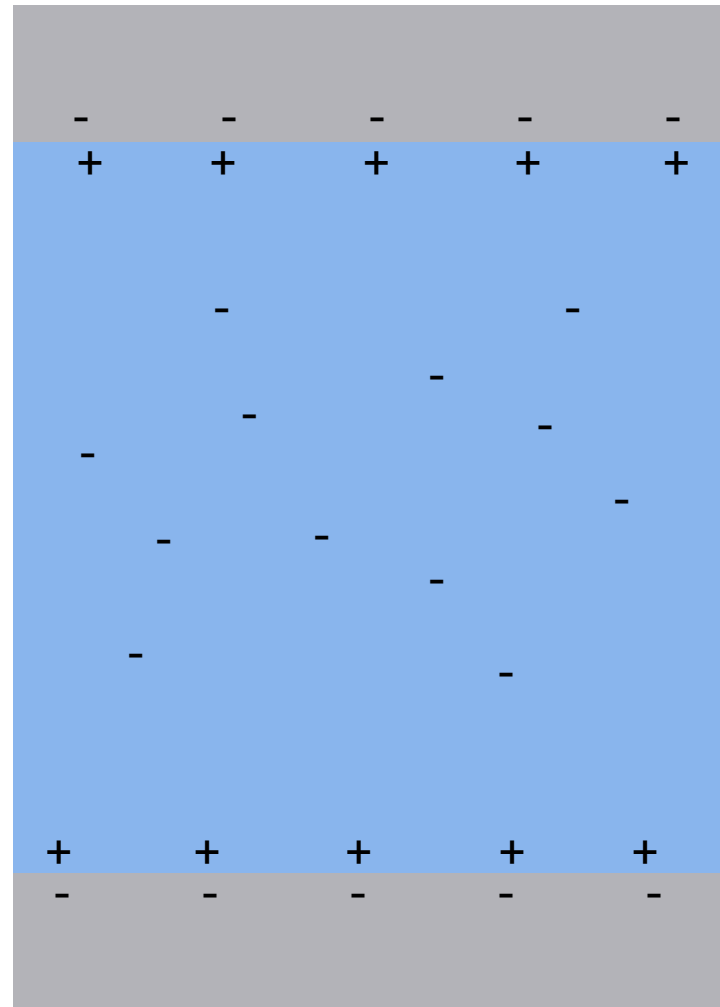


**Overlapping double layers facilitate ion-selective transport.**

# Ion-Selectivity in Nanopores

- Controlling factors
  - Pore diameter
  - **Solution concentration**

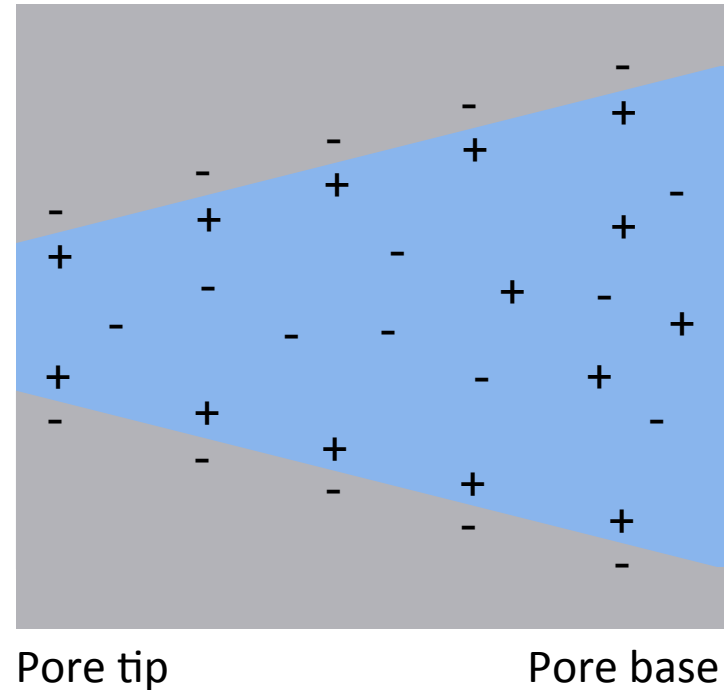
At low concentrations, diffuse layer is quite large – larger nanopores allowed.



# Ion-Selectivity in Nanopores

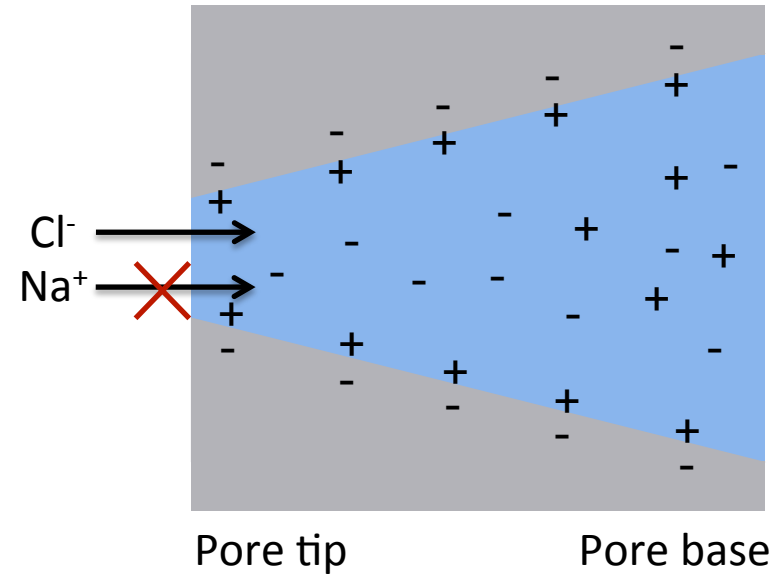
- Controlling factors
  - Pore diameter
  - Solution concentration
  - **Shape**

**For conical pores, selectivity is controlled by concentration at pore tip.**

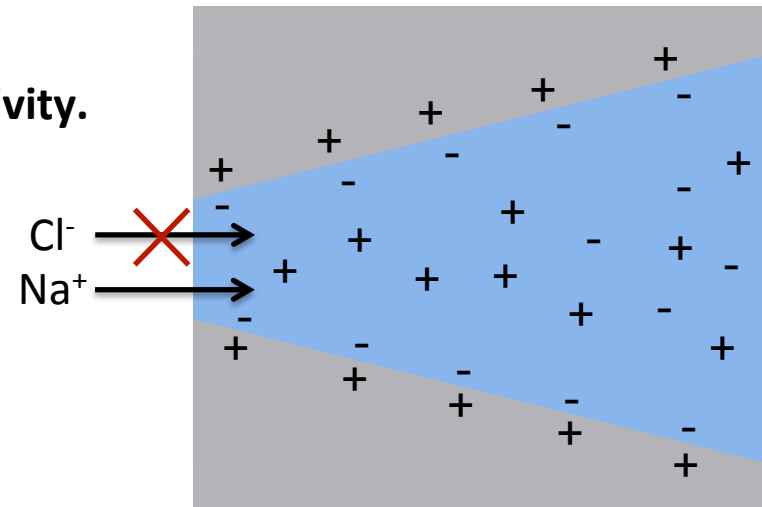


# Ion-Selectivity in Nanopores

- Controlling factors
  - Pore diameter
  - Solution concentration
  - Shape
  - **Surface charge**



Switch surface charge to switch ionic selectivity.



# Switchable Surface Charges

- pH
  - Siwy et al. *Phys. Rev. Lett.* **94** (2005) 048102.
  - Martin et al. *Adv. Mater.* **13** (2001) 1351-1362.
- Light
  - Liu et al. *Chem. Commun.* **49** (2013) 10311.
  - Zhang et al. *Adv. Funct. Mater.* **24** (2014) 424-431.
- Redox active molecules (e.g. ferrocene)
  - Buyukserin et al. *Small.* **3** (2007) 266-270.
  - Elbert et al. *Adv. Funct. Mater.* **24** (2014) 1591-1601.
- Applied Voltage
  - Kang and Martin. *Langmuir.* **17** (2001) 2743-2759.
  - Kalman et al. *Anal. Bioanal. Chem.* **394** (2009) 413-419.

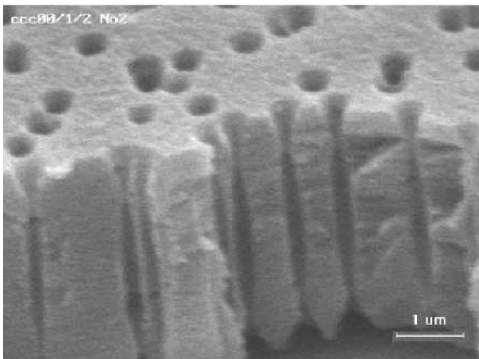
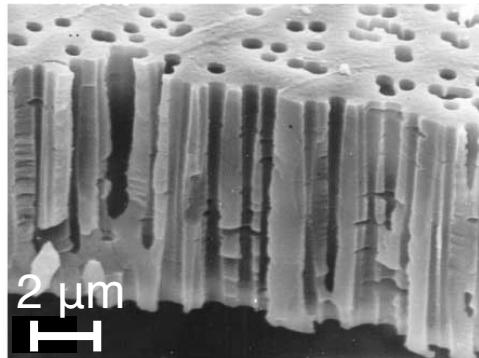
Our Goal:

Electrochemically switch surface charges between ***chemically stabilized states***, rendering a continuously ***applied gate voltage unnecessary***.

# Ion-tracked Polymer Membranes

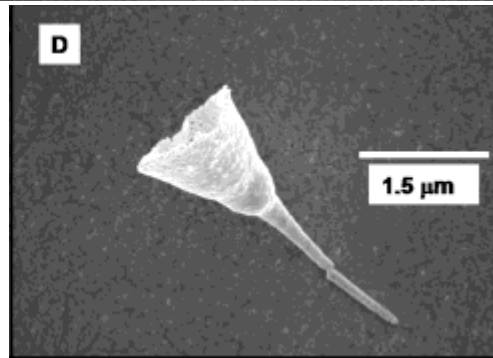
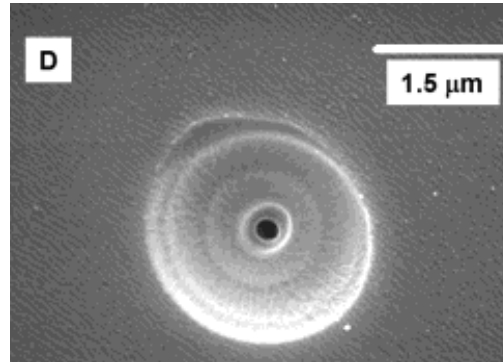
- Polycarbonate films 5-10  $\mu\text{m}$  thick
- Irradiated with Au-ions at 11 MeV
- Ion tracks chemically etched

## Surfactant-assisted etch



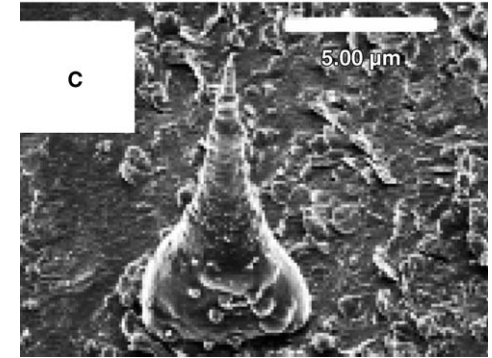
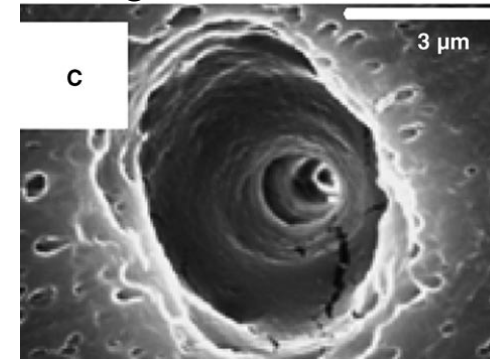
P. Apel. *Rad. Meas.* **34** (2001) 559-566.

## Plasma etch



N. Li *et al.* *Anal. Chem.* **76** (2004) 2025-2030.

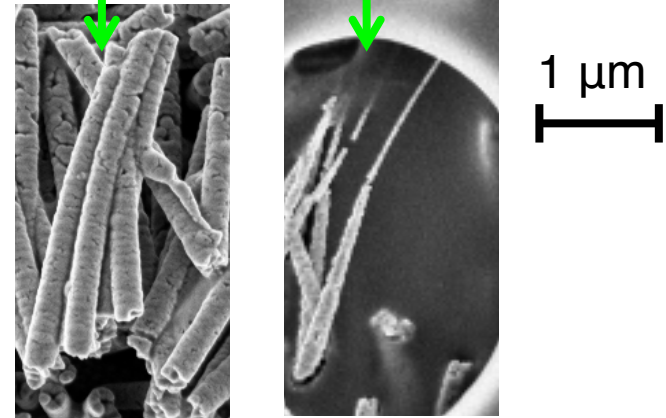
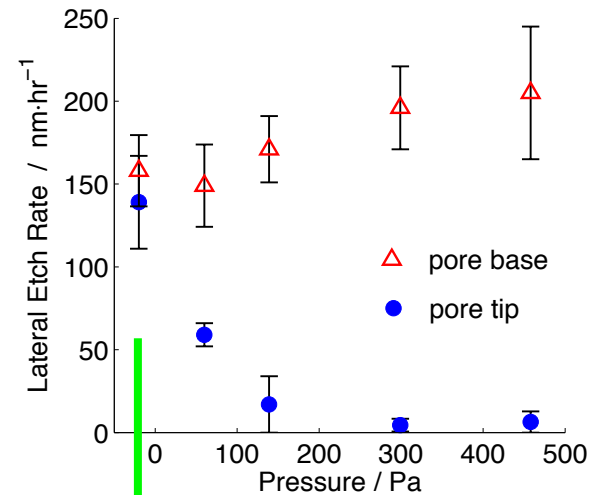
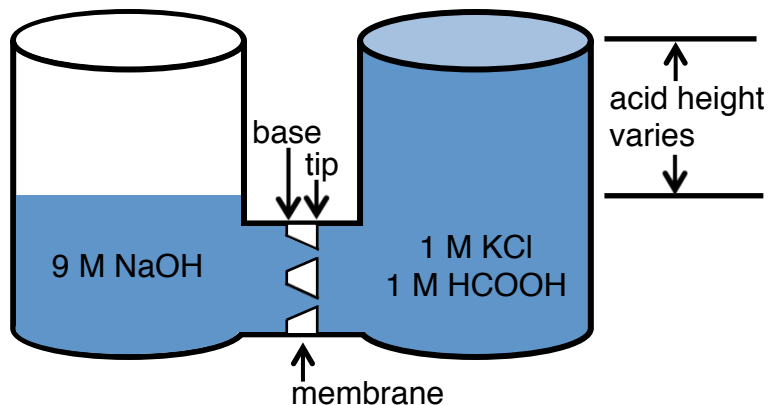
## Voltage-controlled etch



C. Harrell *et al.* *Small.* **2** (2006) 194-198.

# Pressure-Biased Etching

- Ion-tracked polycarbonate membrane separates
  - 9 M NaOH – etchant
  - 1 M HCOOH + 1 M KCl – neutralizer
- Control pressure head to vary concentration gradient of etchant in nanopores



Nickel replicas of conical pores etched 1.5 hours.

**At  $\geq 300$  Pa, etching of the pore tip is suppressed.**

# Gold Plated Nanopores

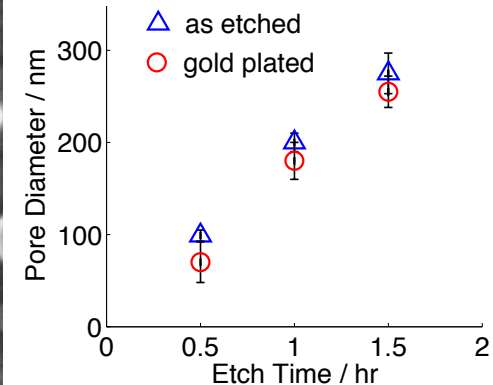
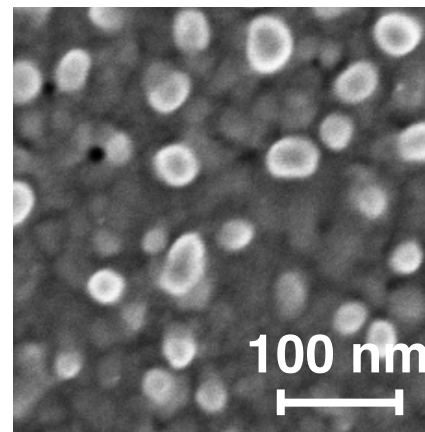
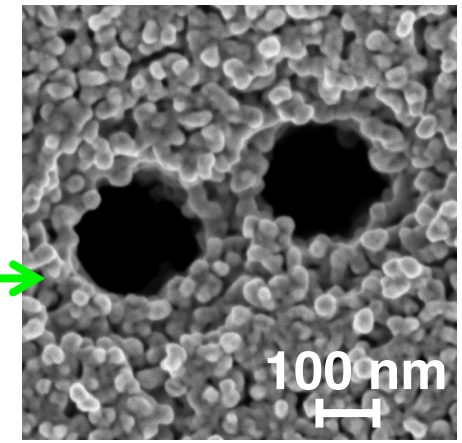
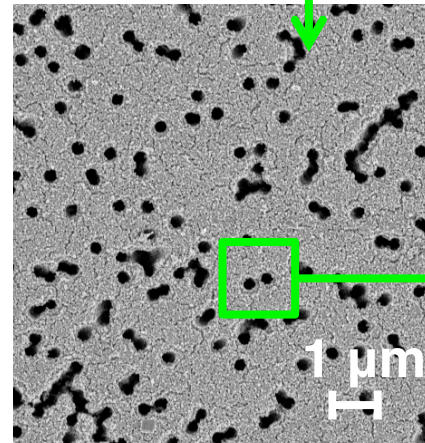
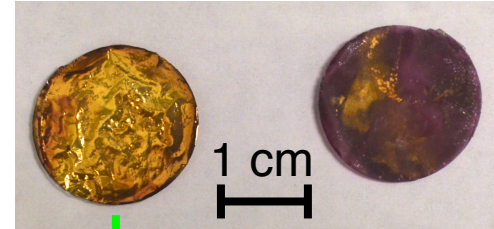
## ■ Electroless plating

- Menon and Martin. *Anal. Chem.* **67** (1995) 1920.
- Sensitize in 0.03 M  $\text{SnCl}_2$ , TFA
- Activate in 0.03 M  $\text{AgNO}_3$ ,  $\text{NH}_4\text{OH}$
- Plate in Oromerse Part B

## ■ To improve uniformity

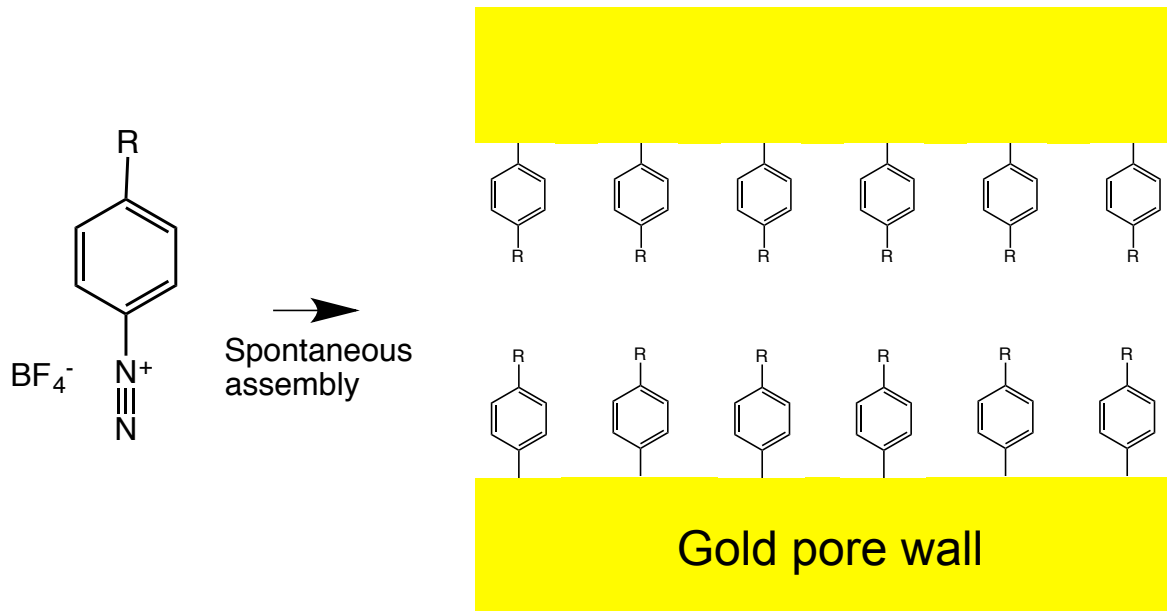
- UV-ozone clean
- Ultrasonic agitation during sensitizing and activation

**Gold is electrolessly deposited along membrane faces and pore walls.**



# Surface Functionalization

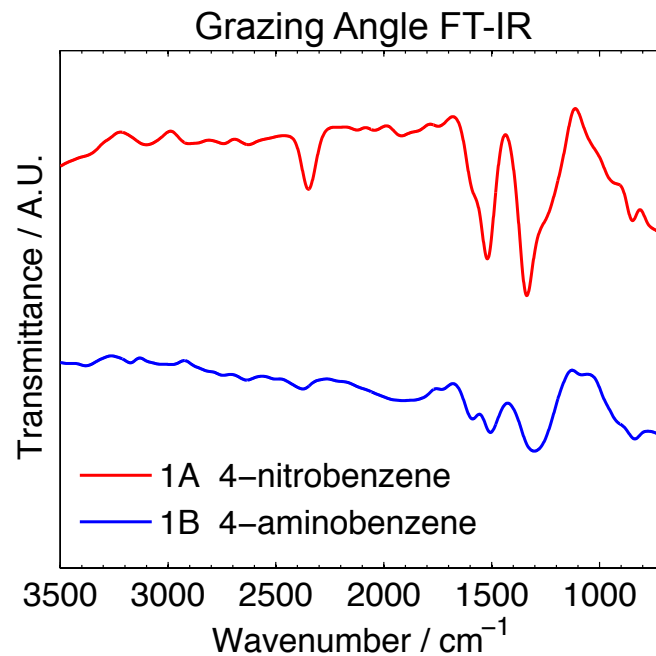
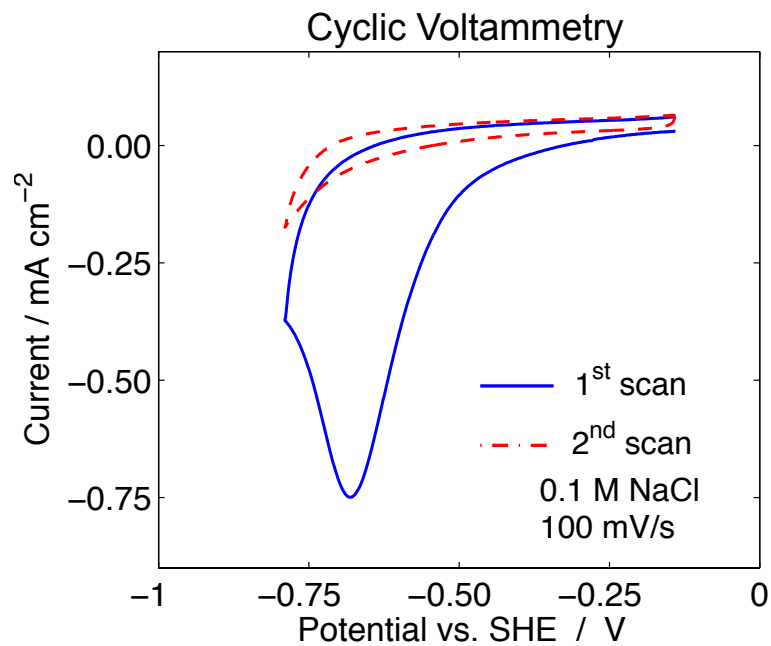
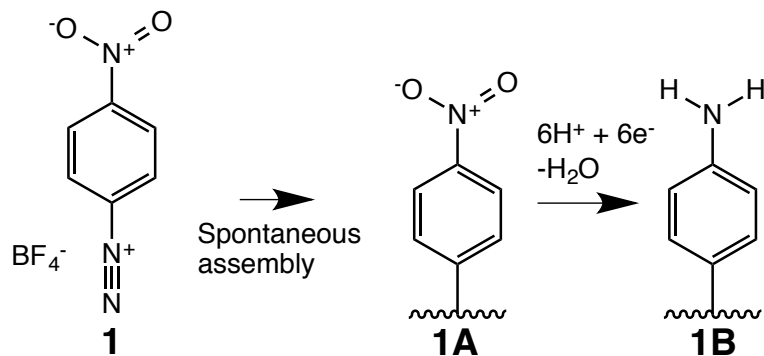
- Spontaneous assembly of diazonium salts
- 1 mM in 1:1 ethanol:water for 4 hours



Our Goal:

Electrochemically switch surface charges between *chemically stabilized states*, rendering a continuously *applied gate voltage unnecessary*.

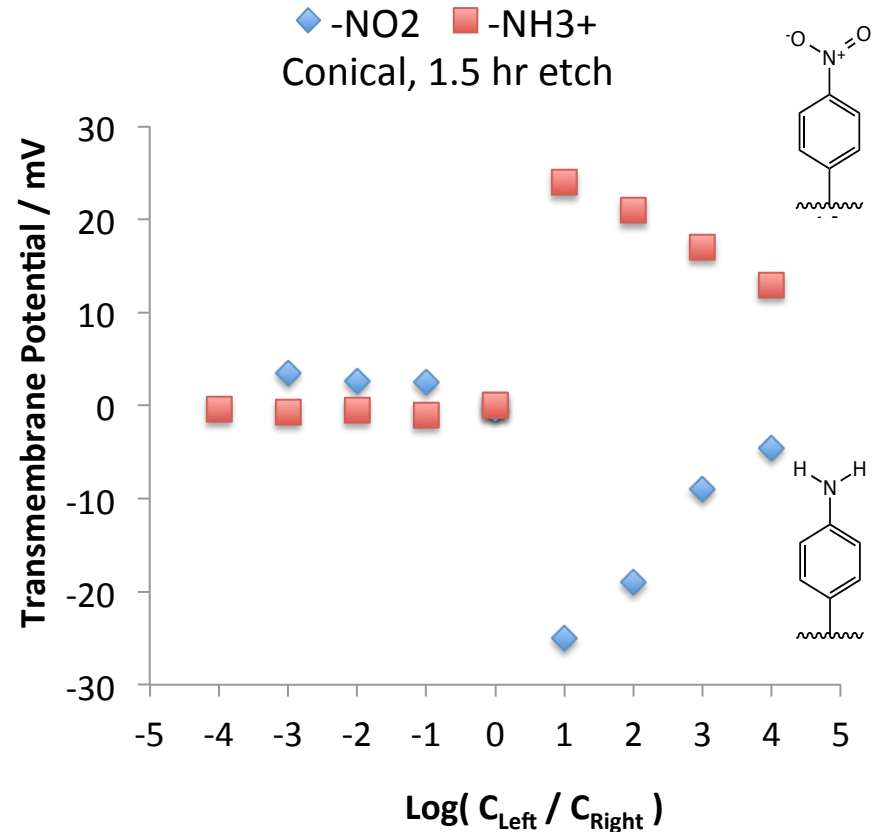
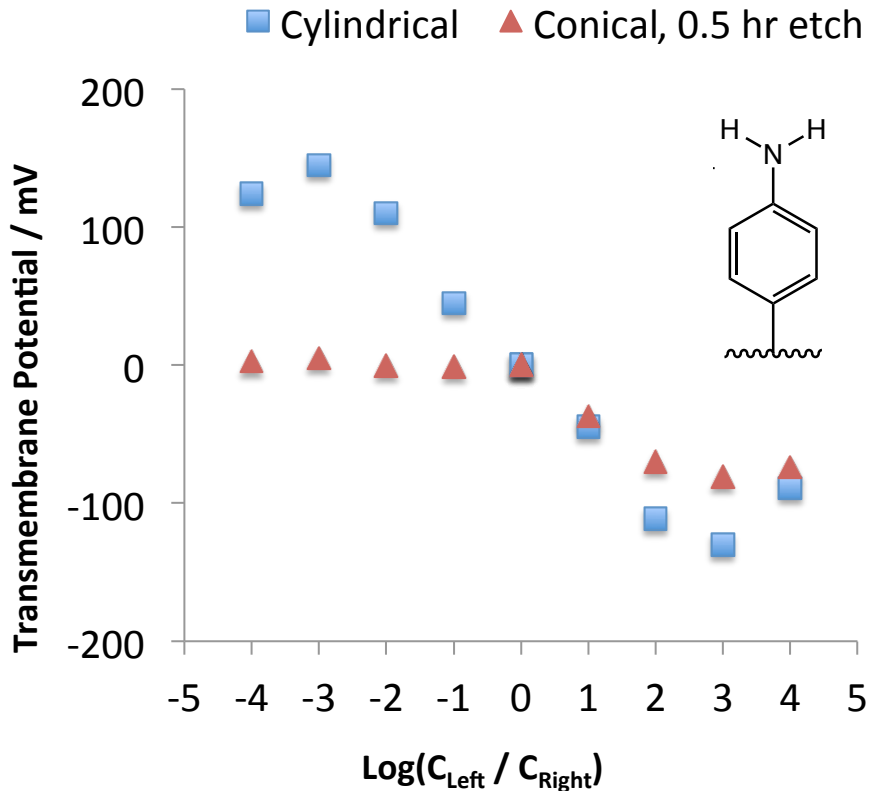
# *p*-Nitrobenzene Diazonium



**Nitrobenzene is spontaneously grafted into nanopores.**

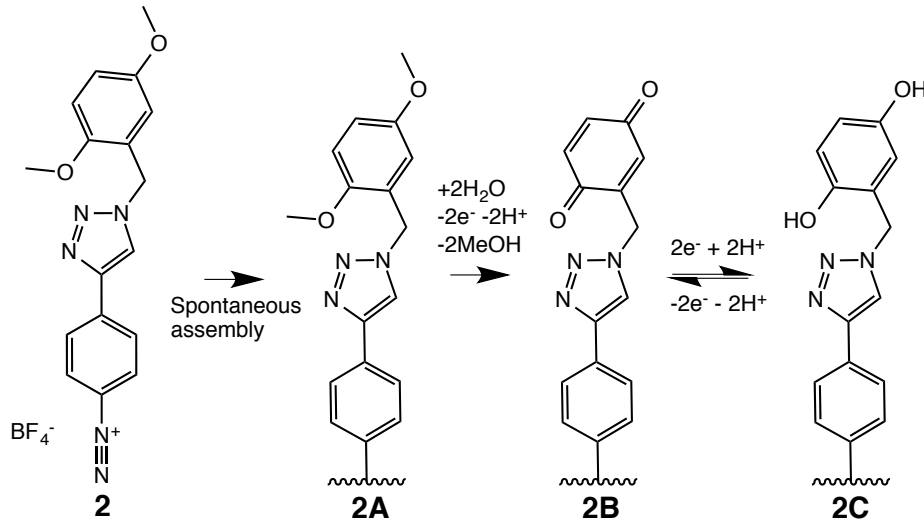
# Ionic Selectivity

0.1 mM – 1 M aqueous NaCl:

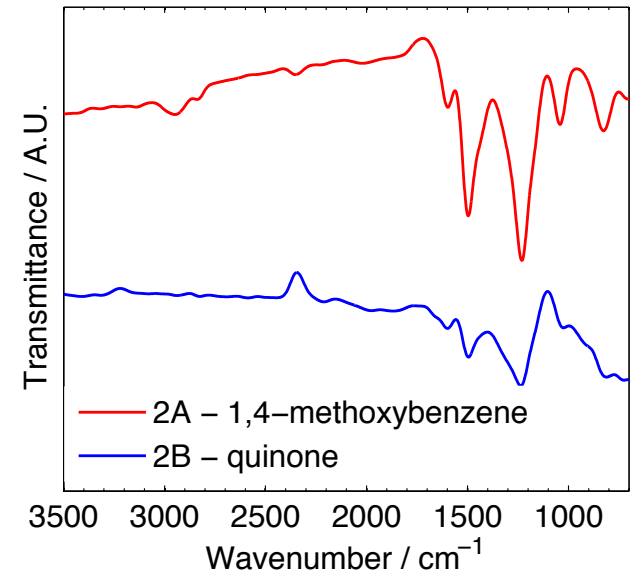
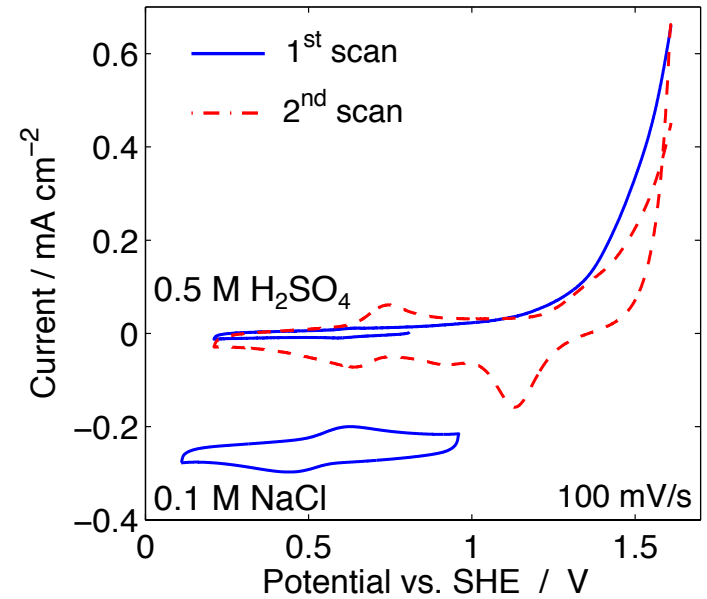


Ionic selectivity of nanopores is *irreversibly* switched upon reduction of nitrobenzene to aminobenzene.

# “Quinone” Diazonium



“Quinone” is spontaneously electrografted into nanopores.



# Looking Forward

- Different chemistries
  - reversible, air-stable
  - electrochemically turn on/or pH-induced selectivity
- Different anions

Questions?