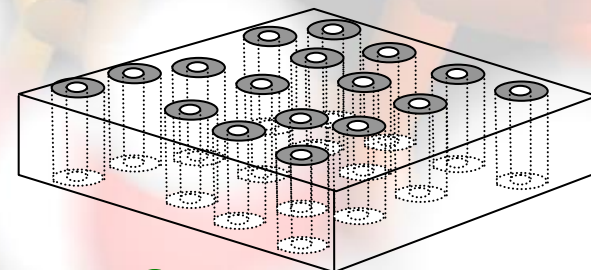


# Active Membrane Systems for the Environment

Bruce Hinds

Univ. of Washington, Mater. Sci. & Engr



- Carbon nanotubes with dramatic flow
- Power efficient electro-osmotic flow through CNTs
- Active gatekeepers and device examples
- Protein pump

Voltage pulsed protein pump *Adv. Funct. Mater.* **2014** in press

Electroosmosis *Nature Nano* **2012** 7(2) 133-139

*CNT flow mechanism* *ACS Nano* **2011** 5(5) 3867-3877

*EO device* *Proc. Nat. Acad. Sci.* **2010** 107(26) 11698-11702

*Fast fluid flow* *Nature* **2005**, 438, 44



MATERIALS SCIENCE & ENGINEERING

UNIVERSITY of WASHINGTON

# Membranes as Materials Engineering Platforms:

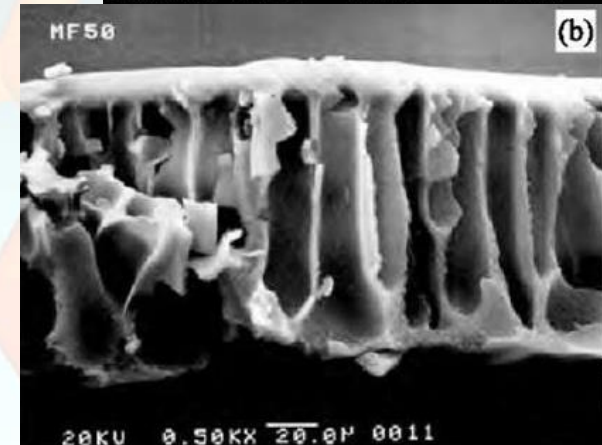
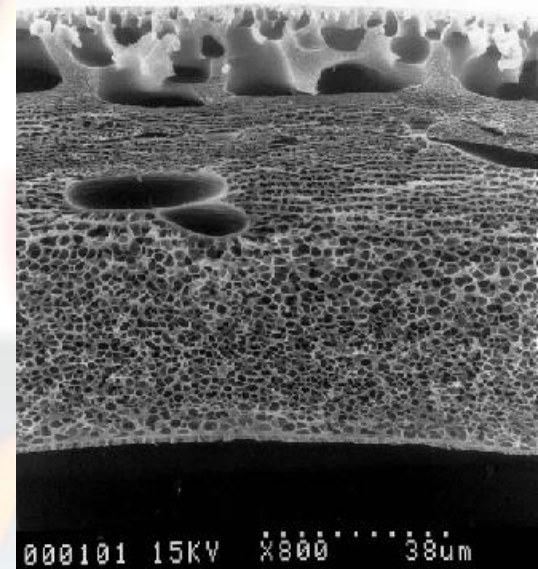
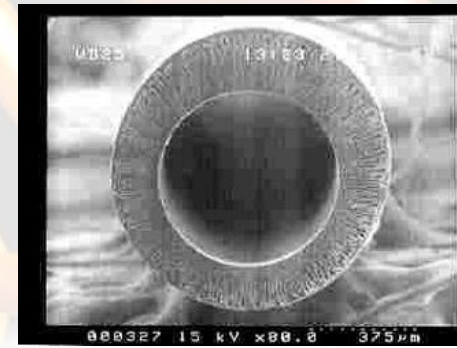
Numerous applications including: water purification, energy separations, environmental separations agriculture, food processing, gas separations, fuel cells, batteries, health care, kidney dialysis ....

## Key Challenges:

Slow speed

Precise chemical selectivity

Fouling



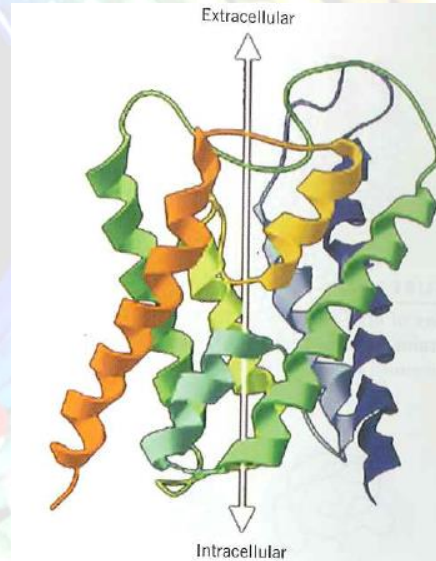
# Protein Channels Basics

**$\alpha$ -type channels** –  $\alpha$ -helices are a common 'scaffold' that gives proteins their form. They are fairly rigid and can be moved like levers. They can also open up the protein structure to form the channel. Known structures have 2-22 of these segments

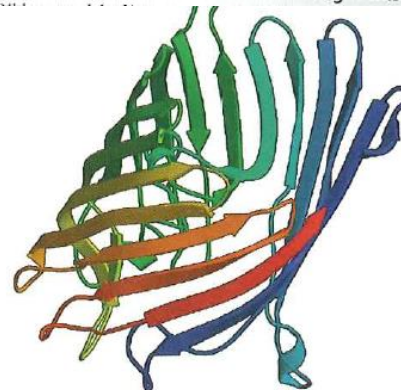
**$\beta$ -barrel channels** -- Sheet like H-bonded structure (not tight helix). They form a barrel of 0.6nm to 3nm in diameter for water channel. Polypeptide loops at the entrance give selectivity. These are associated with simple organisms. The larger channels 2.5-3nm are activated to kill cells (apoptosis).

**Passive Channel** – rely on concentration gradient to transport across the channel. Selectivity is given by chemistry at pore entrance

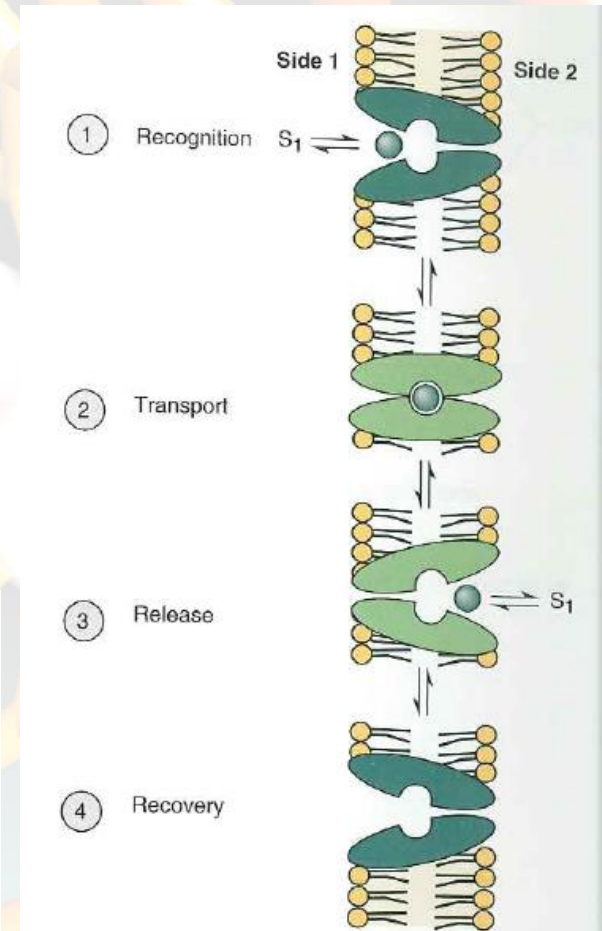
**Active Channels** – Can pump against chemical gradient. Typically use ATP to push alpha helical lever and supply the energy.



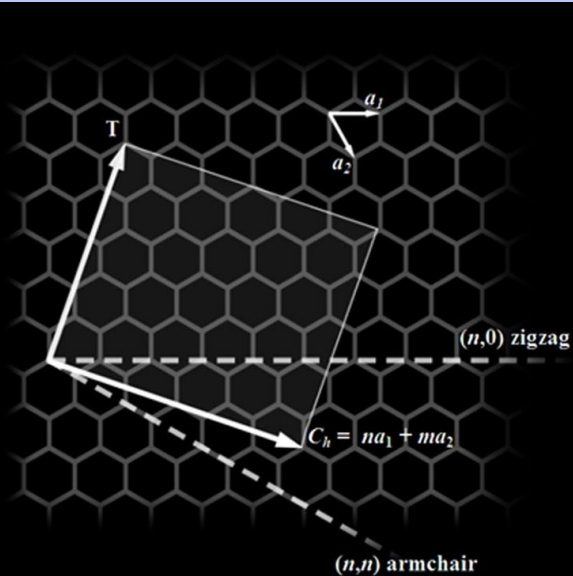
**FIGURE 12.26**  
Multiple  $\alpha$ -helical transmembrane segments.



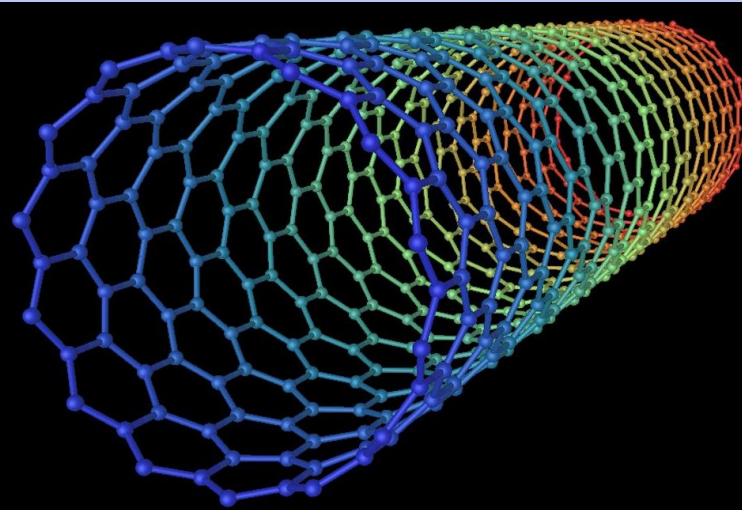
**FIGURE 12.34**  
**Structure of Ompf porin in a tetragonal crystal form.** The transmembrane segments of the porin are  $\beta$ -helices.  
PDB ID: 10 PF. Cowan, S. W., Garavito, R. M., Jansonius, J. N., Jenkins, J. A., et al. The structure of Ompf porin in a tetragonal crystal form. *Structure* 3:1041, 1995.



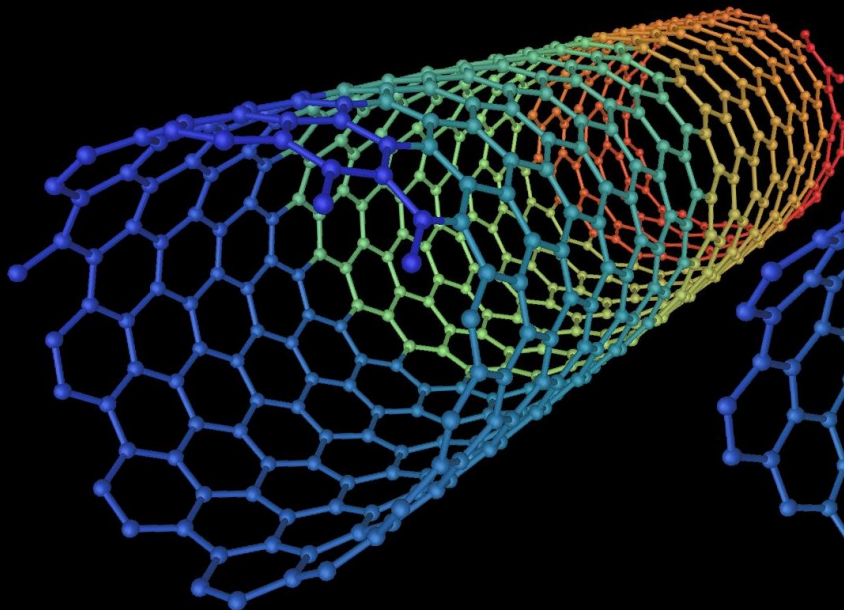
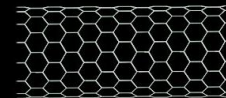
**FIGURE 12.44**  
**Model for a mediated transport system in a biological membrane.** Model is based on the concept of specific sites for binding of substrate and a conformational change in the transporter to move bound solute a short distance but into the environment of the other side of the membrane. Once moved, solute is released from the transporter.



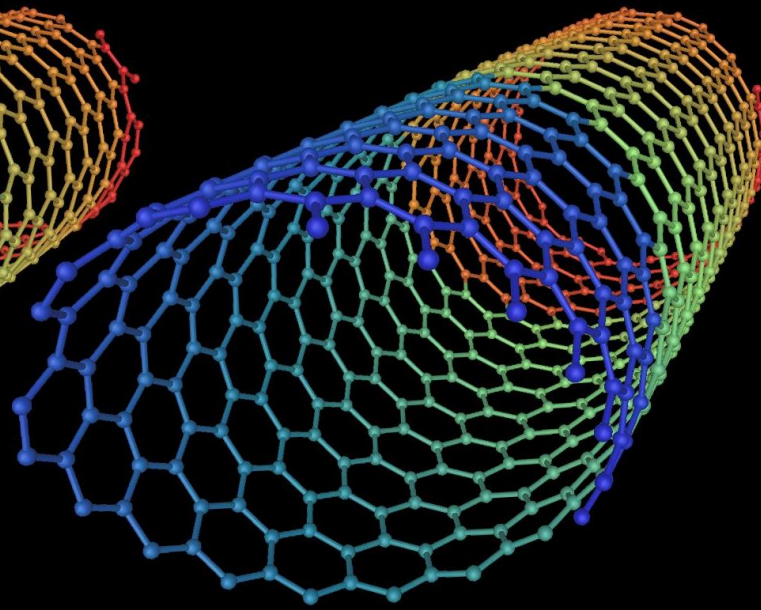
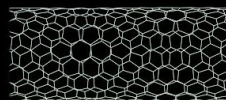
$2n+m=3q$  metallic



$(0,10)$  nanotube  
(zig-zag)



$(7,10)$  nanotube  
(chiral)



$(10,10)$  nanotube  
(armchair)



# Motivation for CNT Membranes

## 3-key attributes unique to CNT membranes:

- \* Atomically flat hydrophobic core
- \* Functional chemistry by necessity at cut entrances
- \* CNTs are conductive

## My key research objectives:

- \* Prove transport through the membranes is through the CNT cores
- \* Understand basis transport phenomena
- \* Demonstrate 'gate keeper' separations that can ultimately solve selectivity/flux problem
- \* Take advantage of conductive CNTs to electrostatically modulate pore entrance

## Applications in:

**Chemical separations**

**Catalysis**

**Bio-materials**

**Water Purification**

**FO power generation**

**Energy storage**

**Programmable drug delivery**

The ultimate membranes are found in the walls of every, living cell.

# Approaches to CNT membrane fabrication

## Polymer impregnating aligned MWCNT array

Hinds *et al Science* **303** 62-65 (2004)

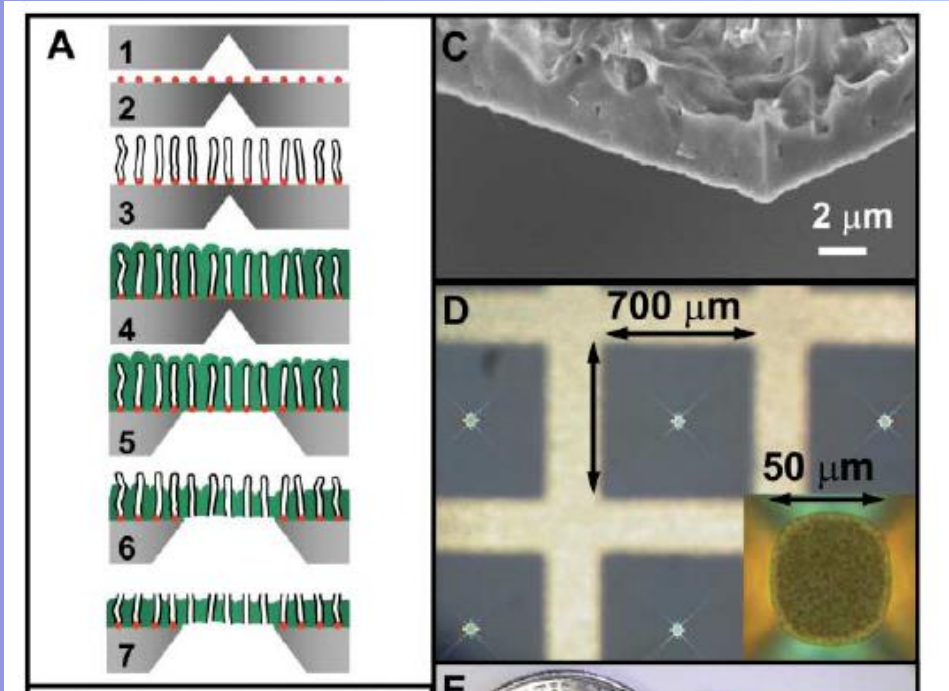
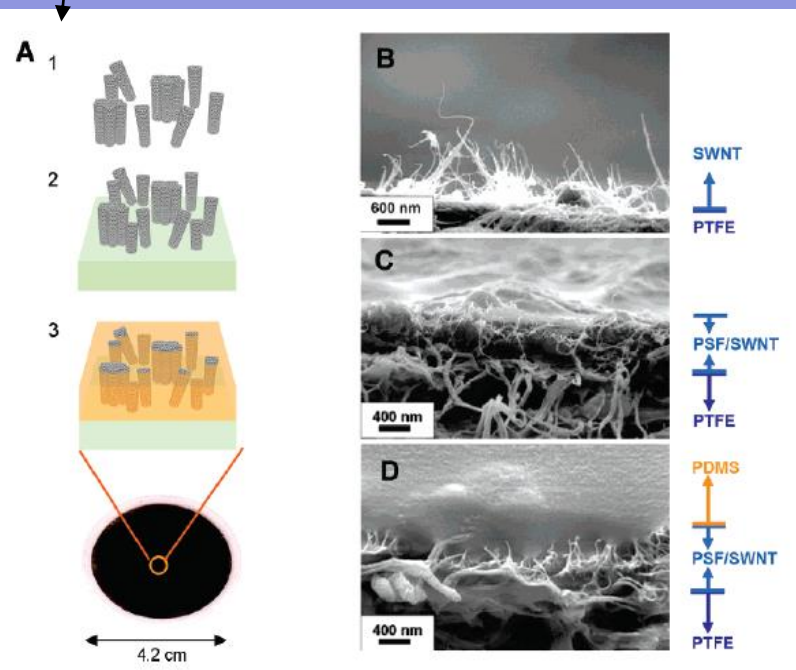
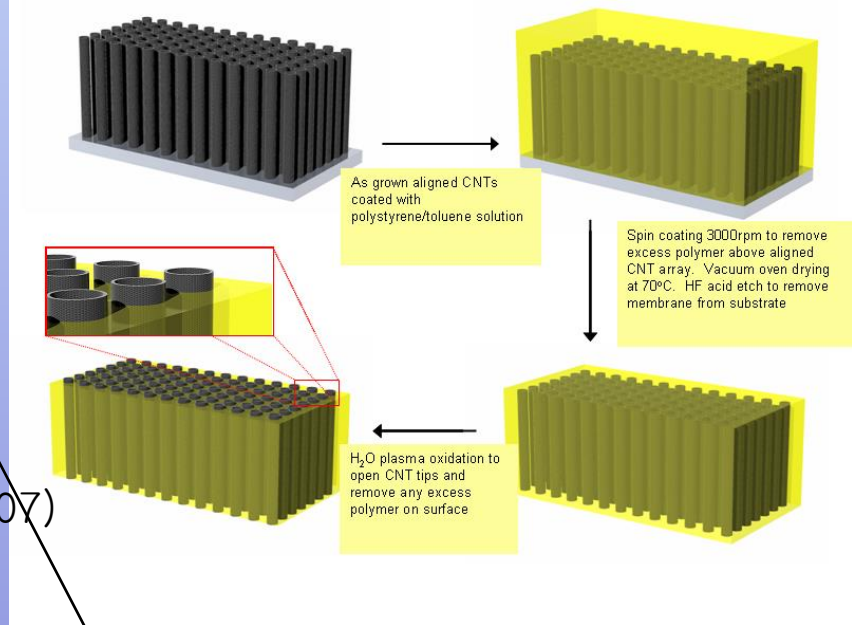
## Si<sub>3</sub>N<sub>4</sub> encapsulation of aligned SW/MW CNTs

Holt (Bakajin) *et al. Science* **312**, 1034-1037 (2006).

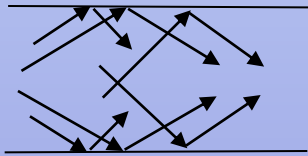
## Polymer impregnation of filtration aligned CNTs

Kim (Marand) *et al. Nano Lett.* **7**, 2806 -2811 (2007)

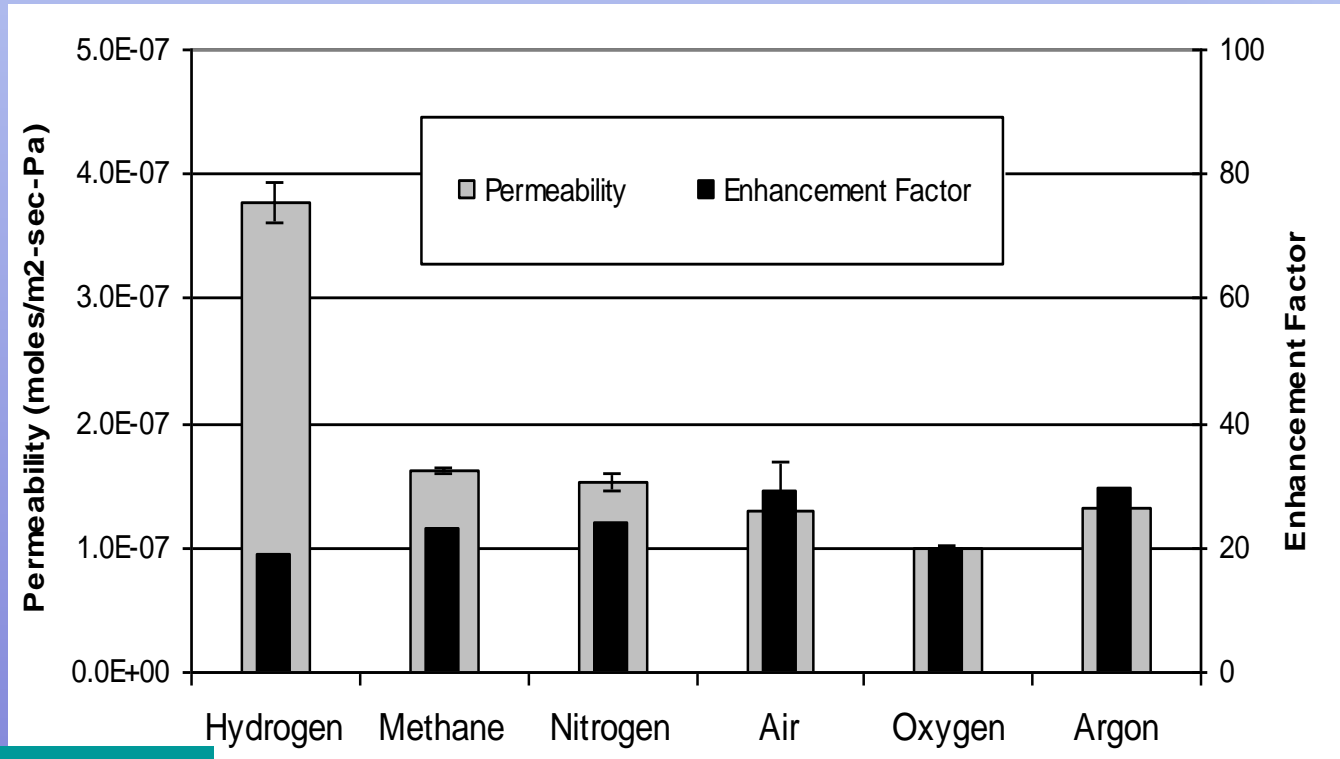
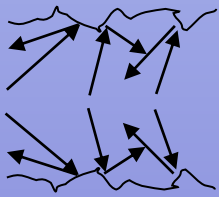
Also Li group Az. St, Noble group UC Boulder



# Gas Permeability of CNT Membrane



VS.



Porosity estimated from KCl Diffusion measurements

*Enhancement factor = Experimental permeability / Calculated Knudsen permeability*

>1 order of magnitude enhancement of flow for most gases

>2 order observed by Holt *et al.* in ~ 2 nm SWNT and DWNT membranes (*Science* May 2006)

# Summary of Liquid Pressure Flow Data

Liquid	Permeable Pore Density (# per cm <sup>2</sup> )	Membrane Thickness (micron)	Initial Permeability (cm <sup>3</sup> /cm <sup>2</sup> -min-bar)	Flow velocity Normalized at 1 bar (cm/s)	Viscosity (cP)	Haagen-Poiseuille Flow Velocity at 1 bar (cm/s)	Slip Length (micron)
Water	1*10 <sup>9</sup>	34	0.58	<b>25</b>	<b>1.0</b>	5.7*10 <sup>-4</sup>	53.6
	3.4*10 <sup>9</sup>	126	1.01	<b>43.9</b>		5.7*10 <sup>-4</sup>	67.3
			0.72	<b>9.5</b>		1.5*10 <sup>-4</sup>	38.9
KCl (0.017M)	3.4*10 <sup>9</sup>	126	1.25	<b>19.6</b>	1.0	1.5*10 <sup>-4</sup>	107.9
EtOH	3.4*10 <sup>9</sup>	126	0.35	<b>4.5</b>	1.1	1.4*10 <sup>-4</sup>	28.1
IPA	3.4*10 <sup>9</sup>	126	0.088	<b>1.12</b>	2	7.7*10 <sup>-5</sup>	12.7
Hexane	3.4*10 <sup>9</sup>	126	0.44	<b>5.6</b>	<b>0.3</b>	5.1*10 <sup>-4</sup>	9.5
Decane	3.4*10 <sup>9</sup>	126	0.053	<b>0.67</b>	0.9	1.7*10 <sup>-4</sup>	3.4

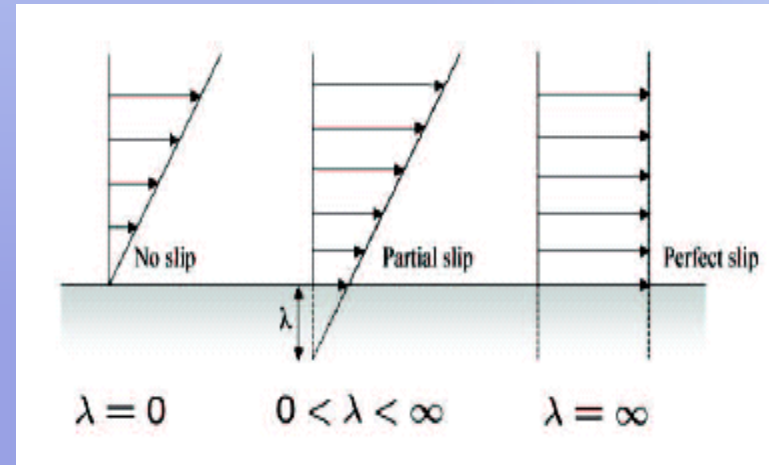
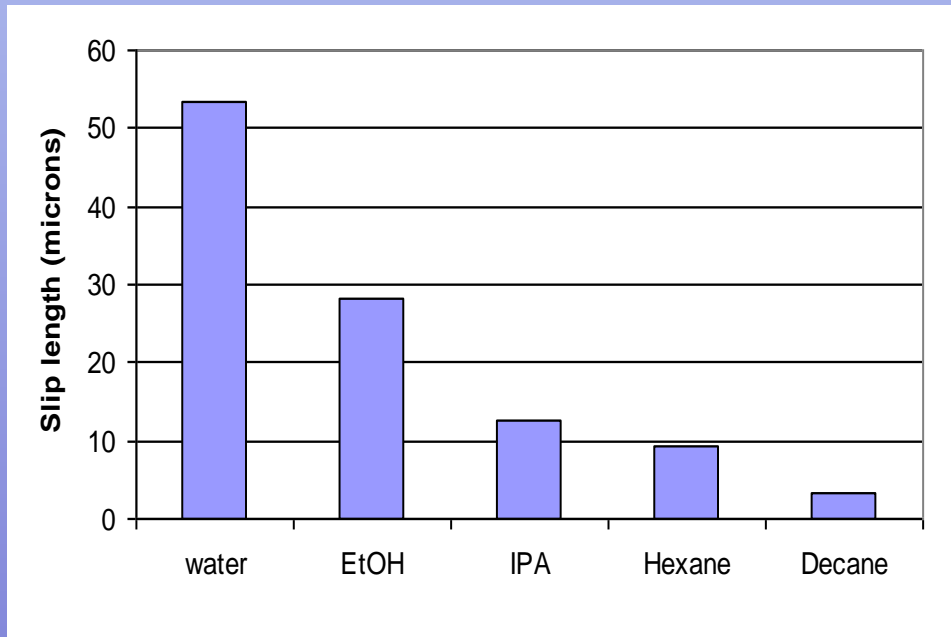
- Flow rates through CNT cores are **4-5 orders of magnitude faster** than simple Newtonian fluids

**Haagen-Poiseuille**  
 $J = (\epsilon r^2 \Delta P) / (8 \mu \tau L)$

**Slip equation**  
 $V(\lambda) / V_{ns} = 1 + 4 \lambda / R$



# Slip Length and the Nature of the Solvents



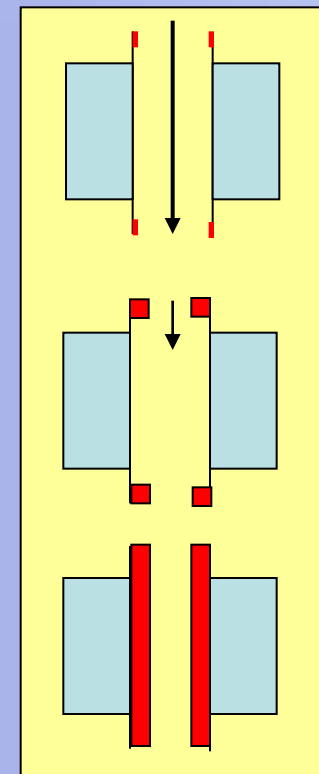
$$\frac{Q(\lambda)}{Q_{NS}} = 1 + \frac{4\lambda}{R}$$

Slip lengths in Carbon nanotubes decrease with increasing hydrophobicity of the solvents (more interaction with CNT)

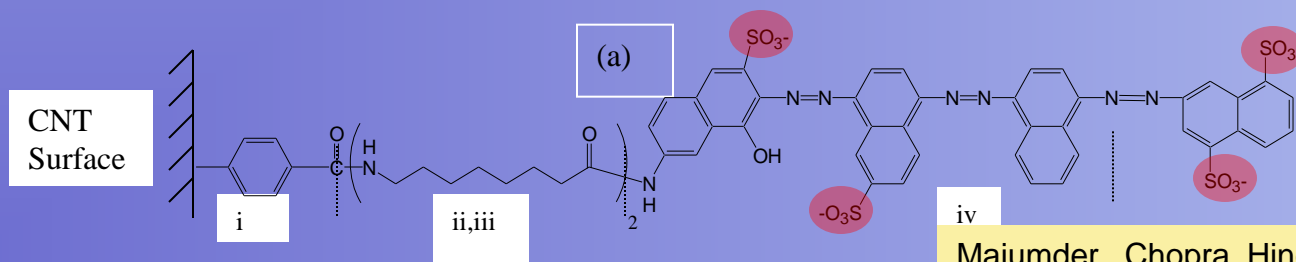


# Chemical modification of CNT core to ruin perfect slip conditions

Chemical Functionalization	Flow Velocity normalized at 1 bar (cm/s)	Enhancement over Newtonian flow	Normalized Diffusive Flux
As made (plasma-oxidized)	10.9(±5.1)	4.6 (±2.1) x 10 <sup>4</sup>	1
Spacer-dye (tip region)	4.7 (±0.7) x 10 <sup>-2</sup>	2 (±0.3) x 10 <sup>2</sup>	0.93
Spacer-dye (core and tip)	< 1.26 x 10 <sup>-3</sup>	< 5.3	1.03



Membranes showed dramatic loss of flow enhancement with chemical functionality but similar ionic diffusive flux. Confirms slip boundary condition. Conclusive evidence against cracks. Electrochemical grafting only on CNTs



Grand intellectual Challenge:  
High flow and selectivity,  
Nature does it all the time

# Why Are Carbon Nanotubes Fast Transporters of Water?

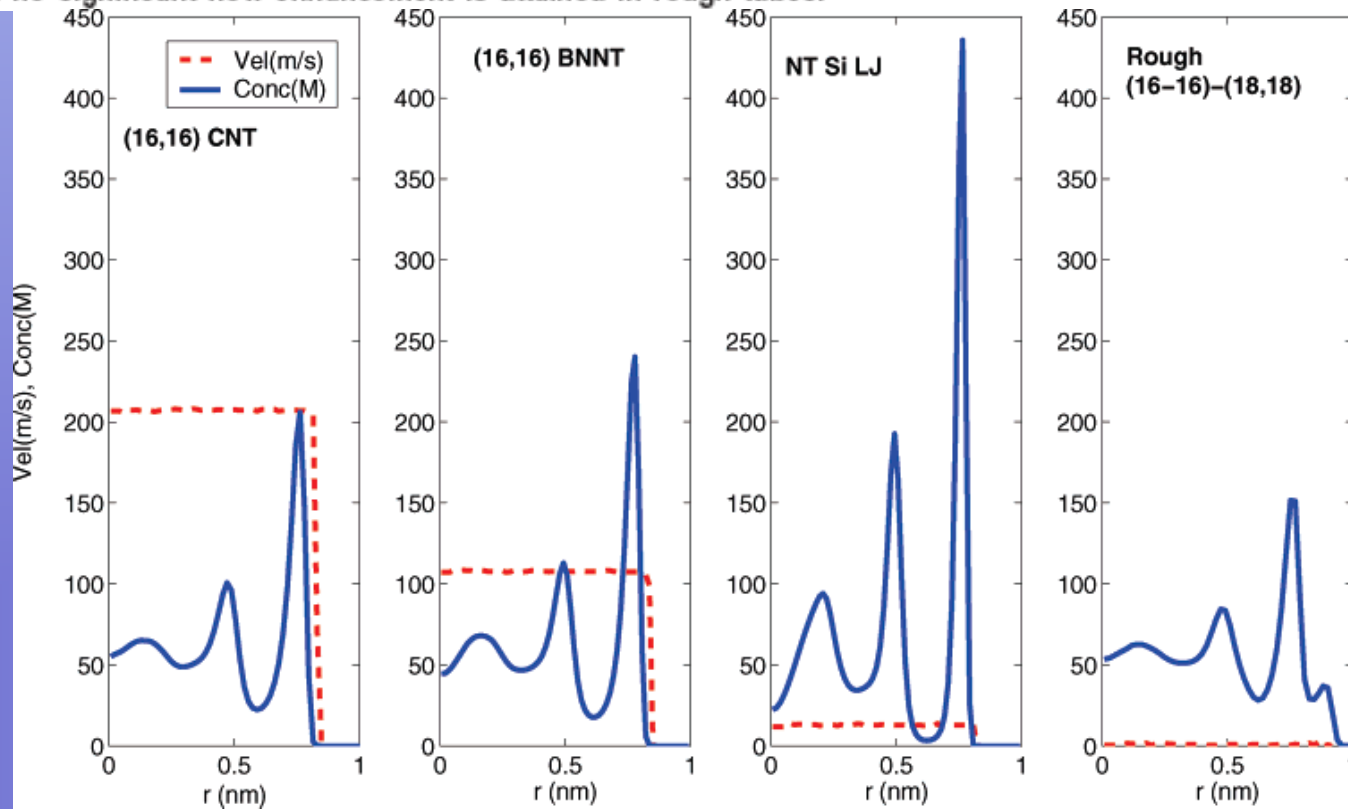
Sony Joseph and N. R. Aluru\*

NANO  
LETTERS

2008  
Vol. 8, No. 2  
452–458

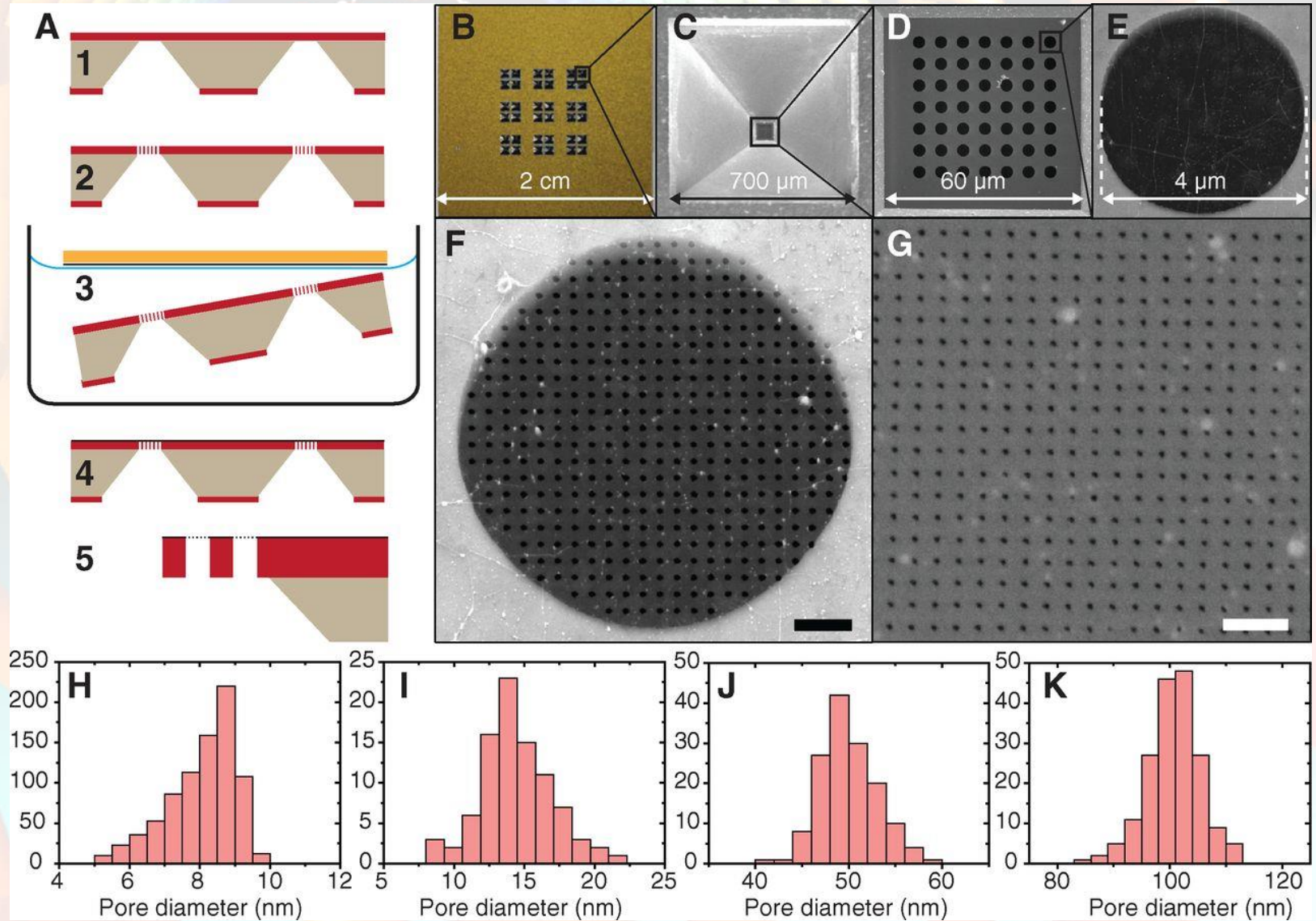
## ABSTRACT

Extraordinarily fast transport of water in carbon nanotubes (CNTs) in recent experiments has been generally attributed to the smoothness of the CNT surface. Using molecular dynamics simulations we investigate water flow in (16,16) CNTs and show that the enhanced flow rates over Hagen–Poiseuille flow arise from a velocity “jump” in a depletion region at the water nanotube interface and that the water orientations and hydrogen bonding at the interface significantly affect the flow rates. For nanotube with the same smooth wall structure but with more hydrophilic Lennard-Jones (LJ) parameters of silicon, the enhancement is greatly reduced because it does not have “free” OH bonds pointing to the wall as in CNTs that would reduce the number of hydrogen bonds in the depletion layer. Roughness in the tube walls causes strong hydrogen-bonding network and no significant flow enhancement is attained in rough tubes.



# FIB Perforation of Freestanding Graphene

Hyung Gyu Park ETH Zurich

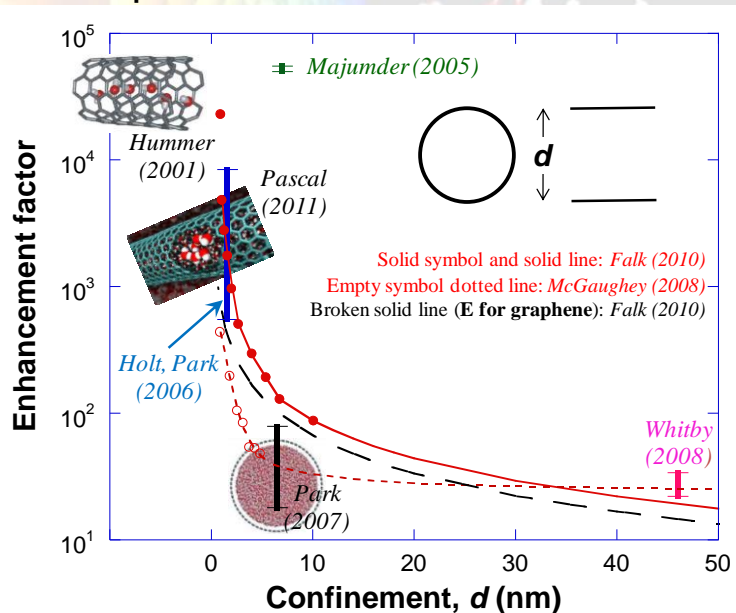


Celebi, Buchheim, Park *et al.*, *Science* (2014)

# Conundrum around Enhanced Water Flows: Enhancement over What?

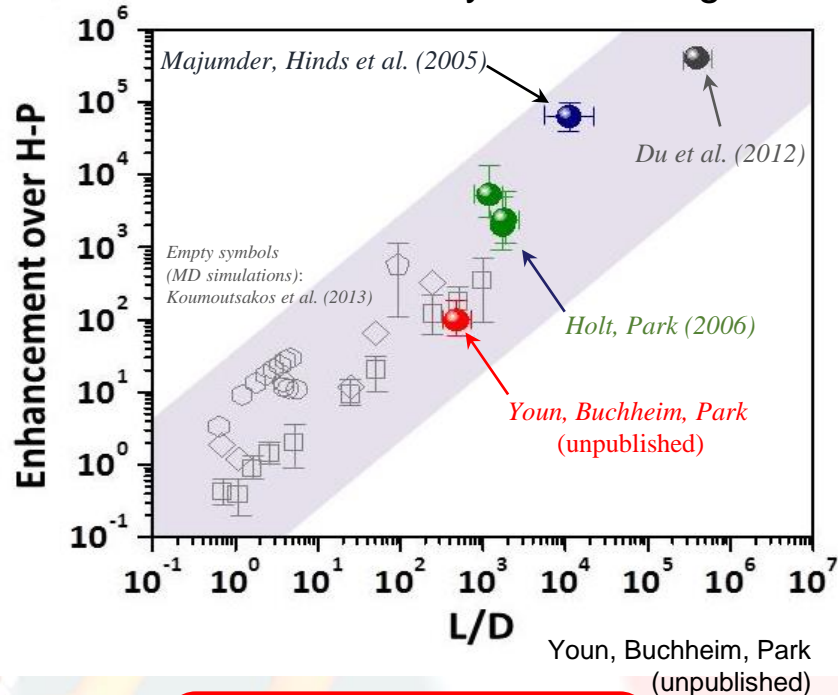


Apparent disagreements between experiments and simulations



Park, Jung, *Chem. Soc. Rev.* (2014)

Reconciliation between experiments and simulations by new scaling

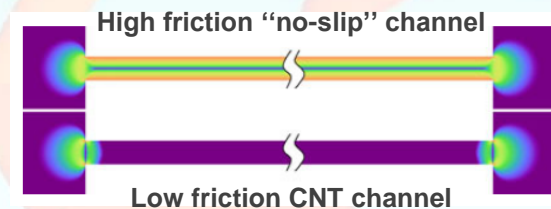


Youn, Buchheim, Park (unpublished)

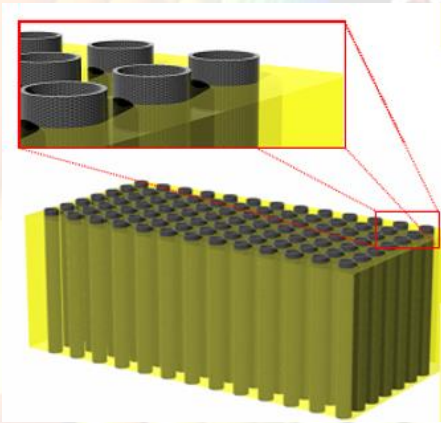
$$EF \equiv \frac{Q_{\text{measured}}}{Q_{\text{H-P}}} = \frac{Q_{\text{measured}}}{\frac{\pi d^4 \Delta p}{128 \mu L}} \approx Q_{\text{measured}} \frac{\mu L}{\Delta p d^4} \propto \frac{L}{d} \Rightarrow EF \propto \frac{Q_{\text{measured}}}{d^3 \Delta p / \mu} \propto \frac{Q_{\text{measured}}}{Q_{\text{Sampson}}}$$

$$Q_{\text{Sampson}} = \frac{\pi d^3}{8 \mu} \Delta p$$

Sampson's formula (1897):  
Solution of the Stokes flow across a pore on a hypothetical 2D disk



# CNT membranes vs Graphene membranes

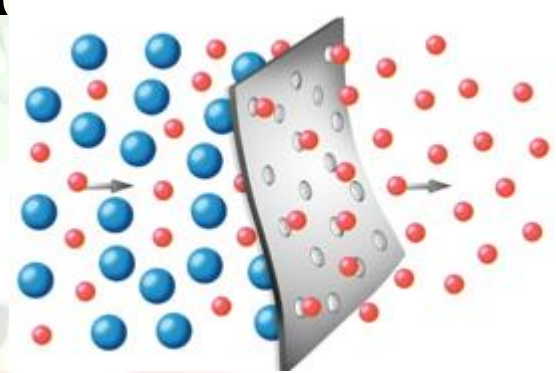


## CNT Pros:

- Chemistry can point up!
- Fast flow through core
- Conductive in insulator with field focus at tip

## CNT cons:

- Very low porosity  $\sim 10^{-4}$
- Still wafer level processing and is a pain
- Interfacial polymerization process generally have CNT lying flat



## Graphene Pros:

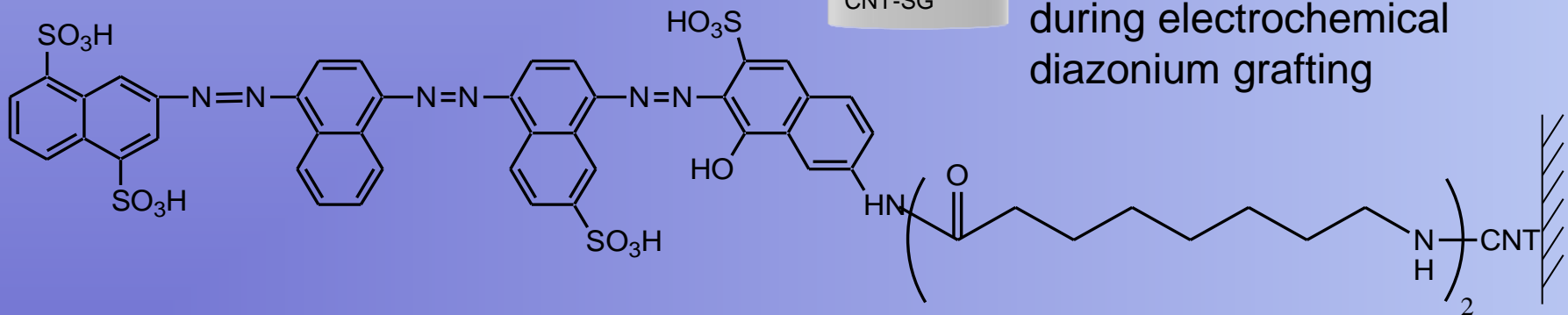
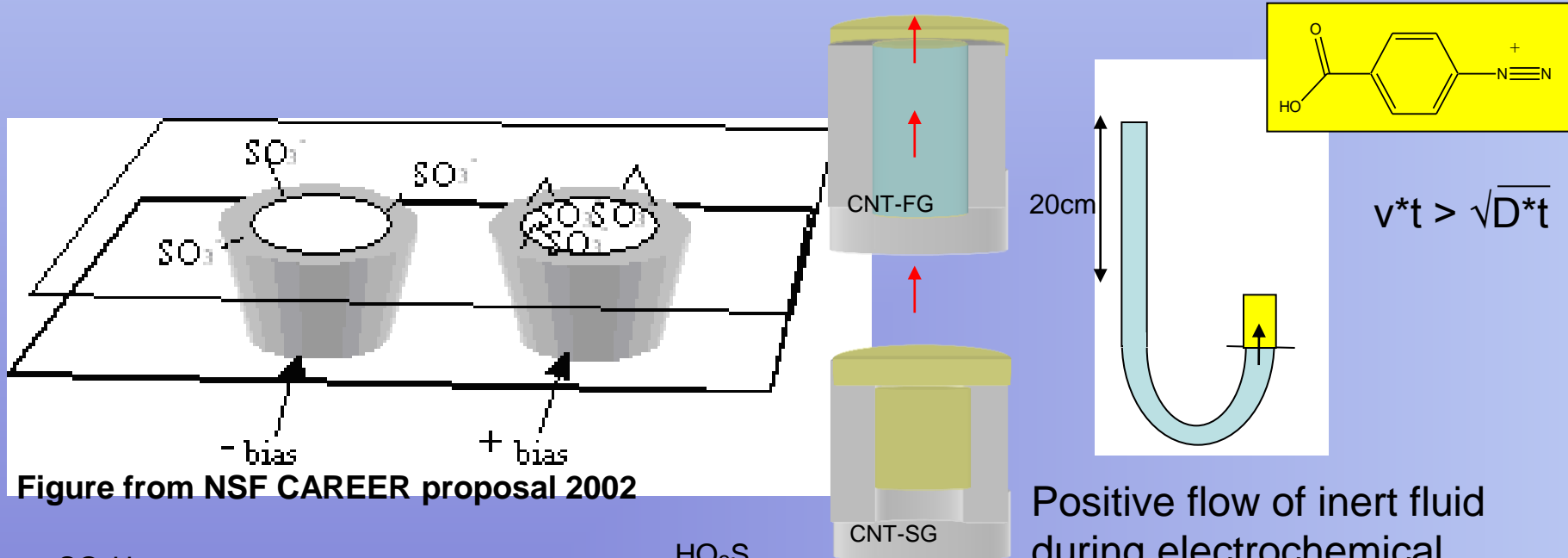
- Atomically thick, ideal limit
- Fast flow through hole
- Conductive

## Graphene cons:

- Processing an even bigger pain
- Defects, defects, defects.
- True intellectual challenge remains to knock out integer #'s of carbons
- Chemistry points in, requiring bigger yet controlled hole

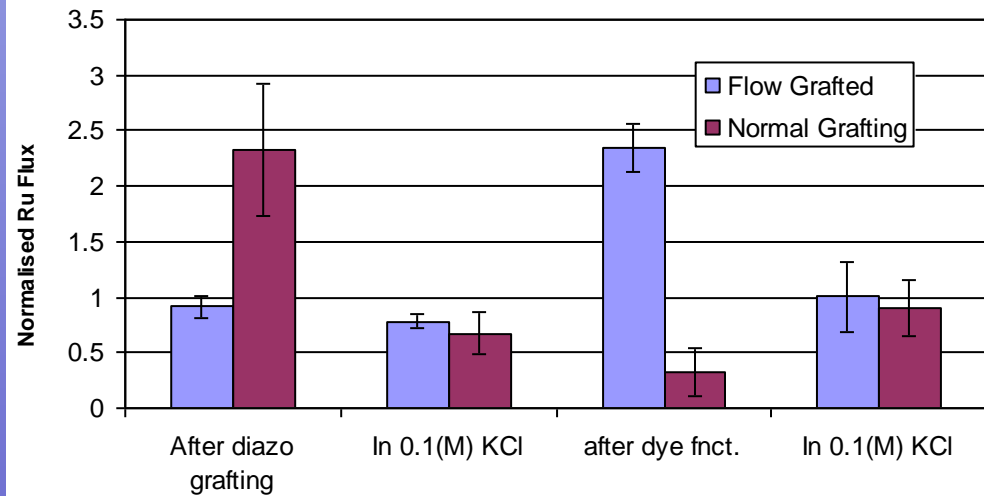
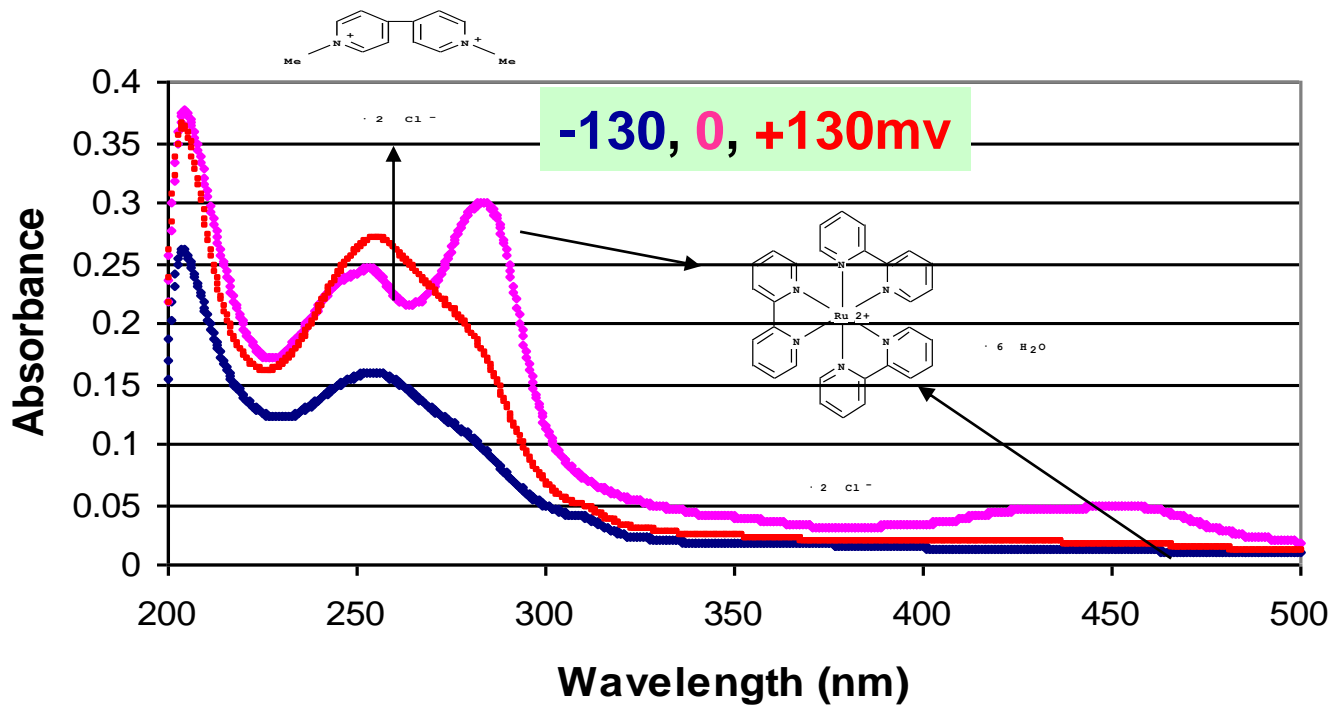
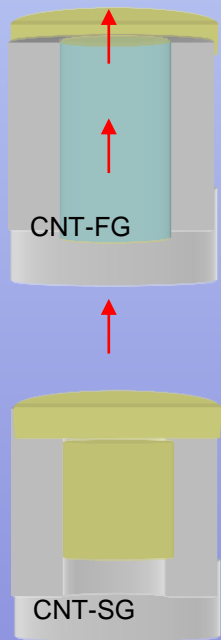
# The next step: active membrane structures

Electrostatically modulated gate keeper ligands at entrance to CNT pore



“Voltage Gated Carbon Nanotube Membranes” Majumder, M.; Zhan, X; Andrews, R; Hinds, B.J \* *Langmuir* **2007** 23, 8624.

# Dramatic Electrostatically Modulated Gatekeepers

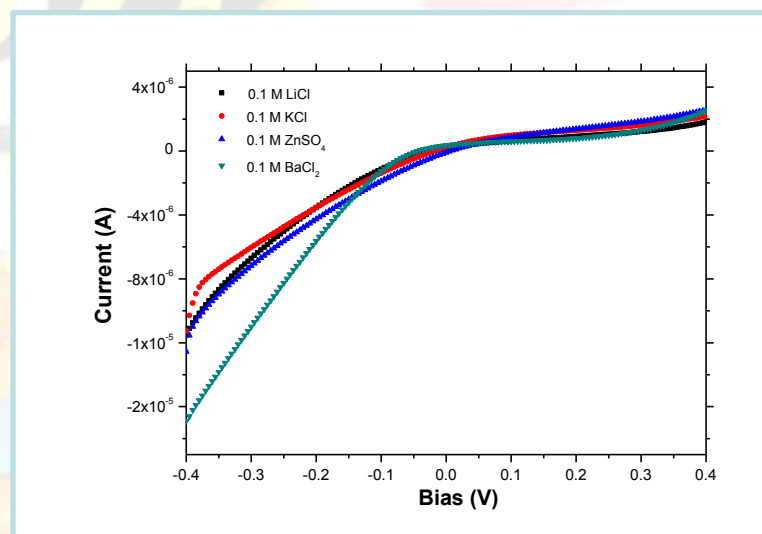
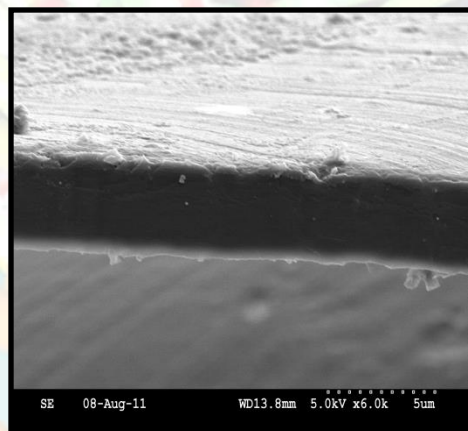
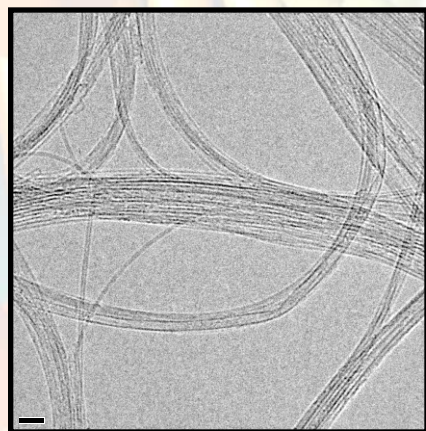
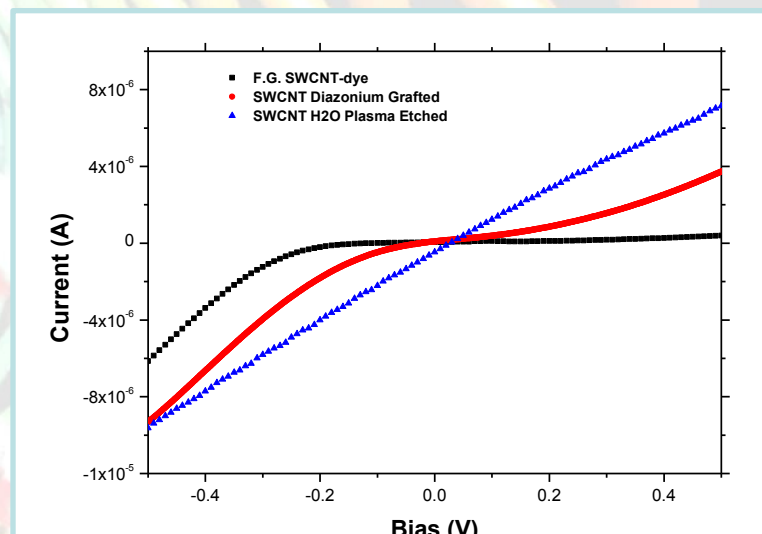
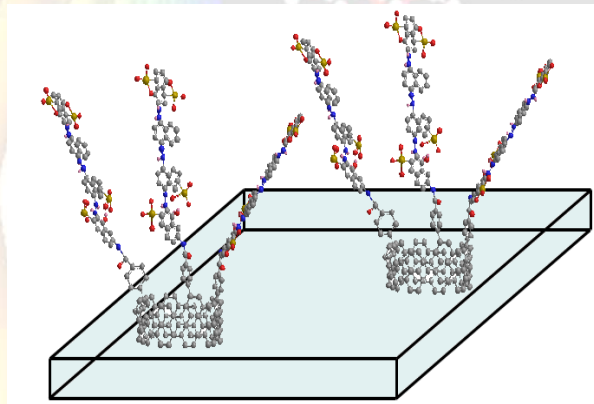


~  $2.4 \times 10^{13}$  sites/cm<sup>2</sup>  
by capacitance measurement  
J. Membr. Sci.

Basis for new NIH R01 grant for  
programmed transdermal drug  
delivery

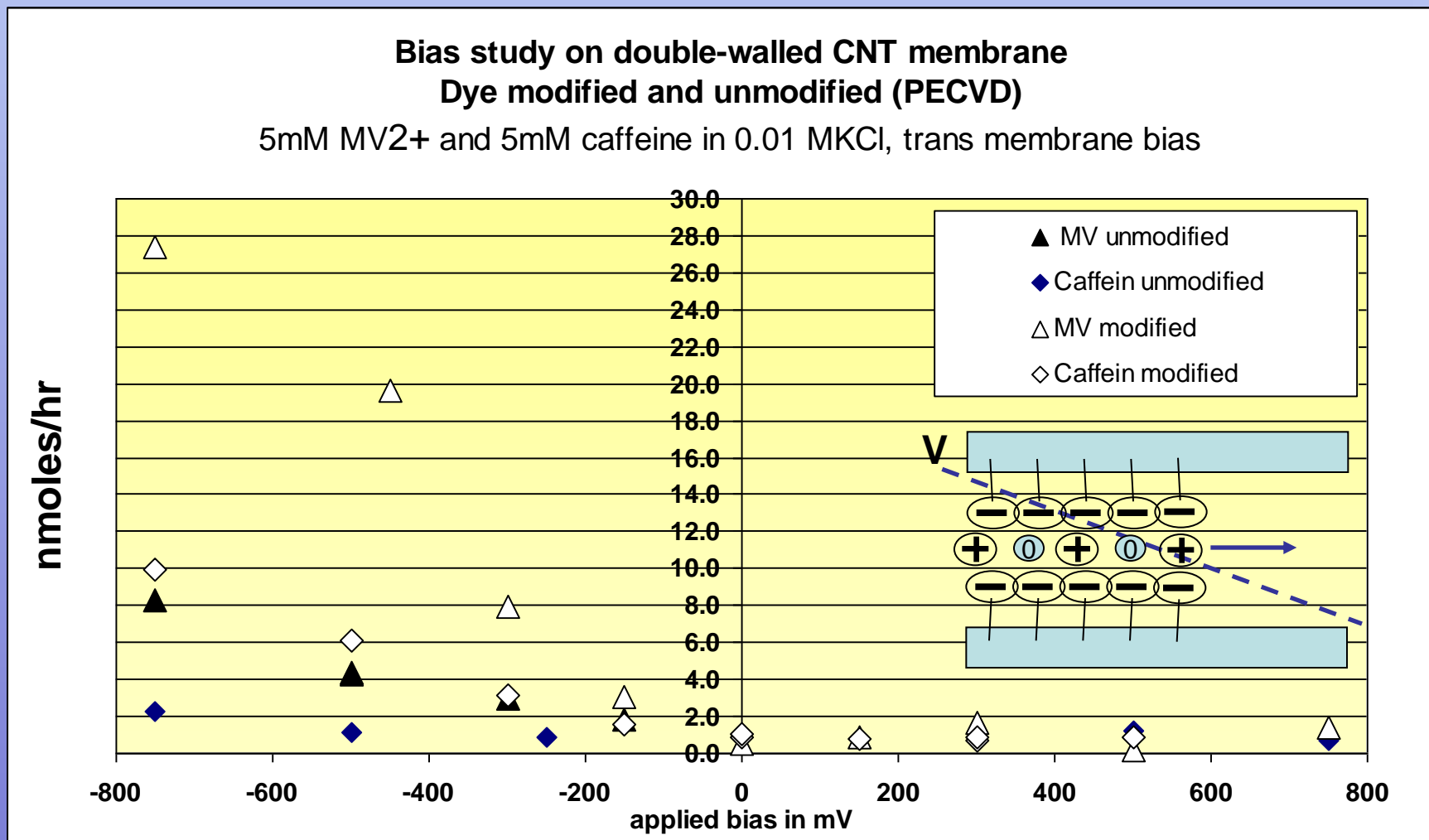


# Small ion blockage by gatekeeper paddles



- By reducing size of CNTs (~1.5nm) and by using SWCNTs and using a long rigid paddle (~1.5nm) we are able to see effective gate keeper rectification current of small ions.
- The structure closely mimics protein channels.

# Electro-osmotic flow through DWCNT membrane



- 10 fold electro-osmotic flow (caffeine) over diffusion
- 20 fold electro-phoretic flow (MV<sup>2+</sup>)

# Observed EO in 1nm SWCNT membranes

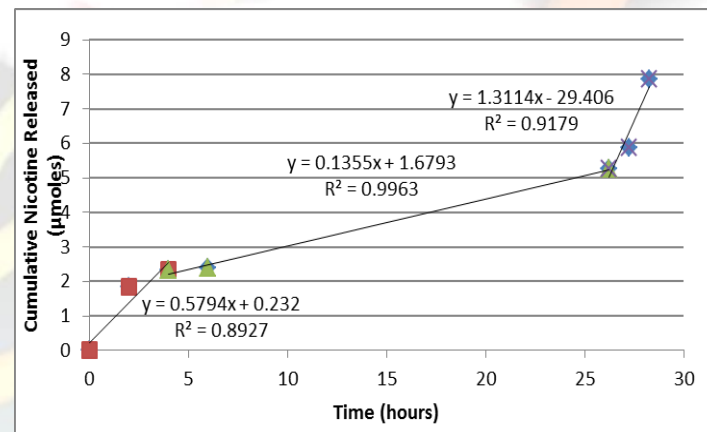


**With electroosmosis giving a 'plug flow' and ions having bulk mobility in the moving frame of reference, dramatic electroosmotic velocities are seen.**

	<b>EO velocity</b>
1nm SWCNT	3 cm/s-V
~2nm DWCNT	0.18 cm/s-V
7nm id MWCNT	0.16 cm/s-V
Anionic AAO	0.0004 cm/s-V

**4 orders of magnitude EO enhancement seen in small SWCNTs without counter ion current. Anion repulsion is 'screened' above 20 mM salt concentration**

# Wireless 'bluetooth' control of nicotine delivery through CNT membrane



Demonstration of wireless control of nicotine delivery based on survey response.

# Electro-catalysis: a responsive membrane frontier

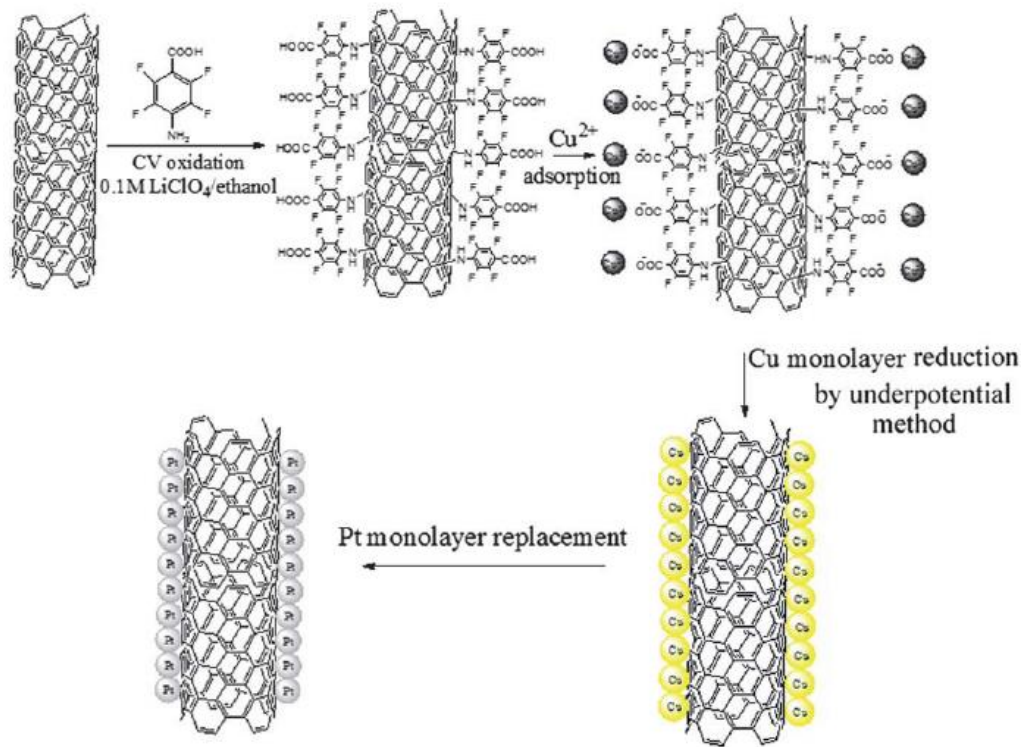


Fig. 1 Schematic illustration of the fabrication procedure for Pt monolayer coating onto MWCNT mattes.

\* World record MeOH Pt mass activity by monolayer Pt/Cu chemistry 2711 A/g

X. Su et al J. Mater. Chem., **2012**, 22, 7979–7984

\* MeOH partitioning to CNT walls for efficient electrocatalysis

J. Goldsmith and B.J. Hinds J. Phys. Chem. C **2011** 115(39)

19158-64

**Can we immitate how enzymes work to precisely orientate substrate to hit the metal center?**

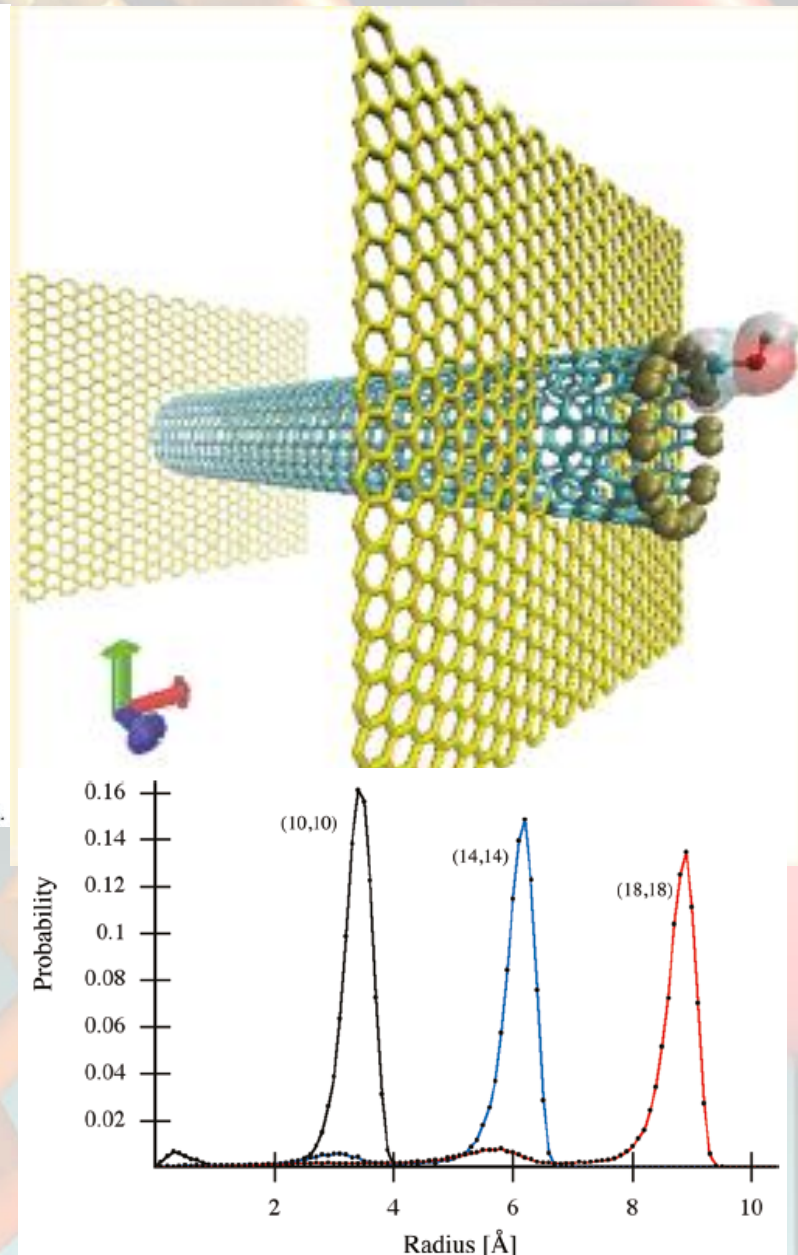
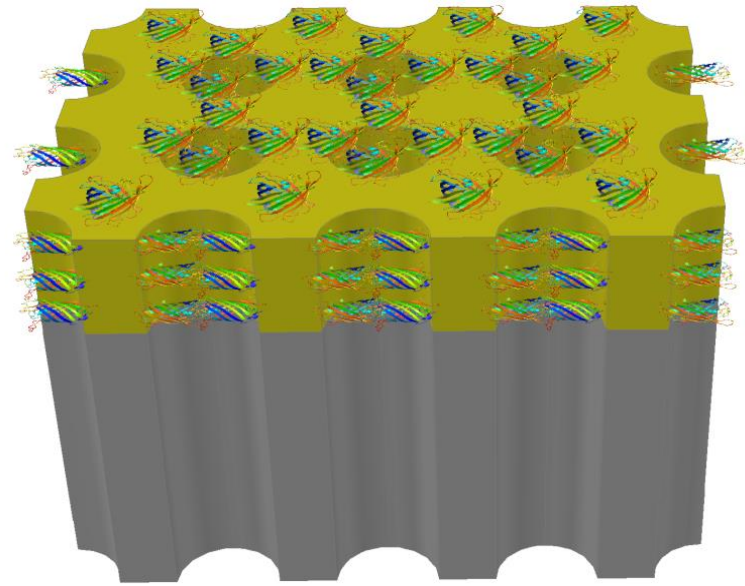
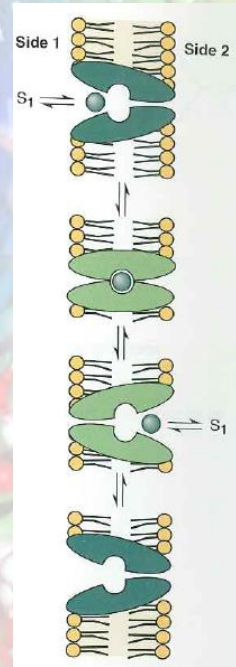
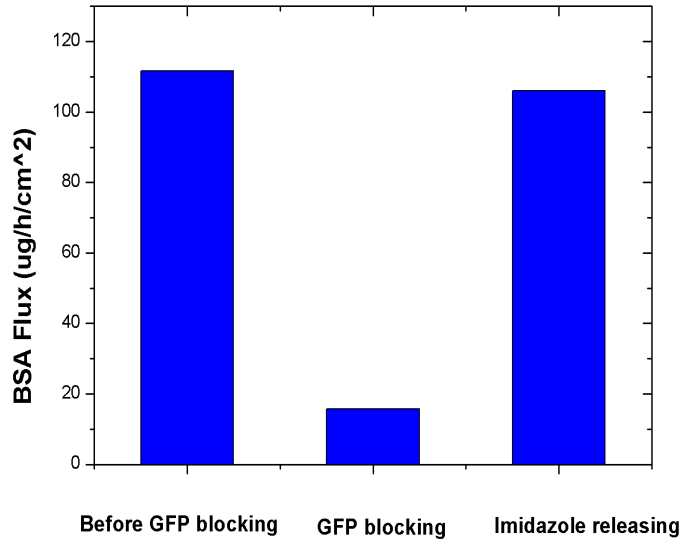


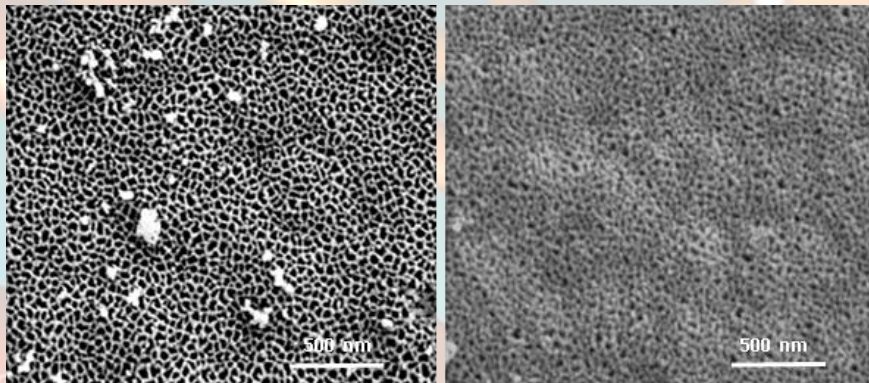
Figure 2. Probability density function for the radial position of methanol's carbon ( $f_i = 0.15$ , Pt charged). Zero is the center of the CNT pore.

# New Directions in Actively Pumping Membrane Systems



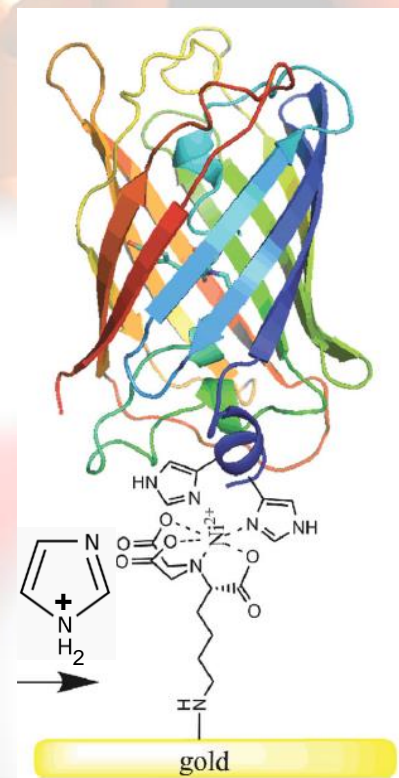
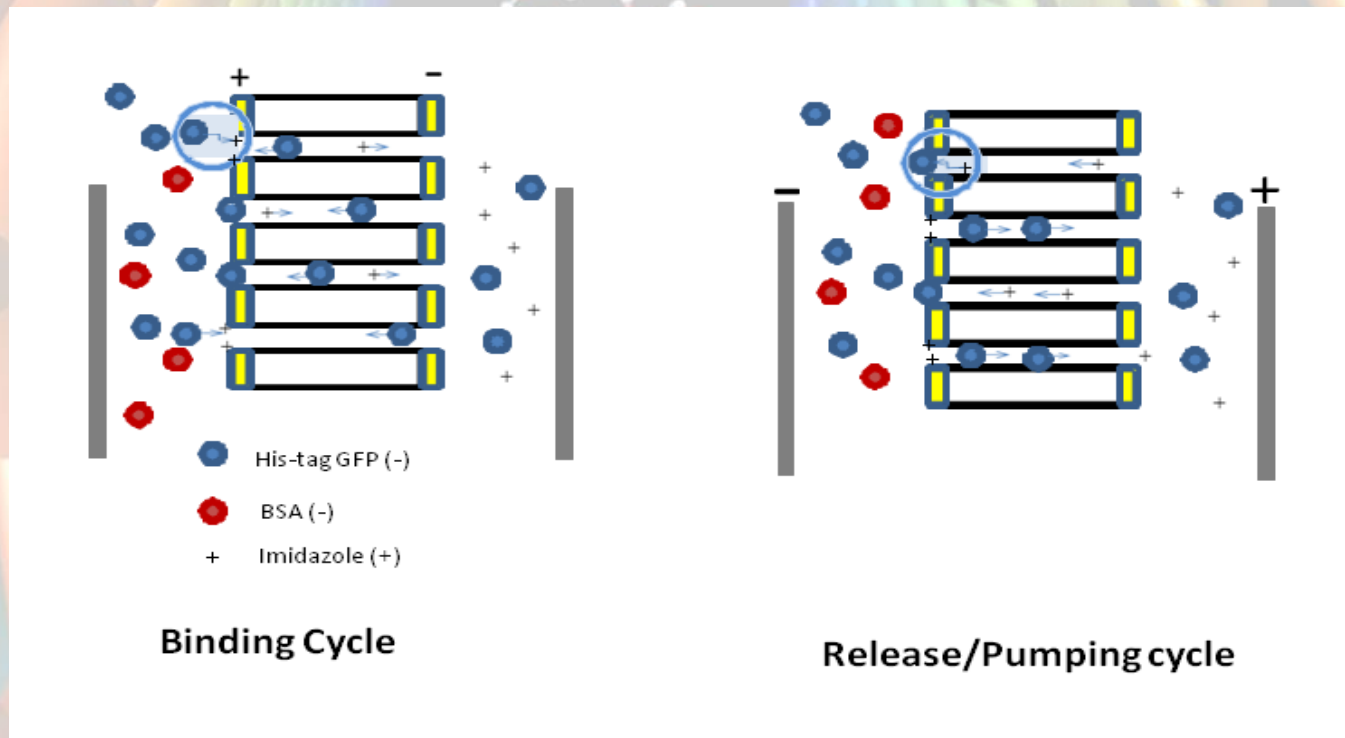
Electrophoretic pumping flux of BSA before, after his-tagged GFP blocking and imidazole releasing

Schematic of AAO membrane blocked by his-tagged GFP



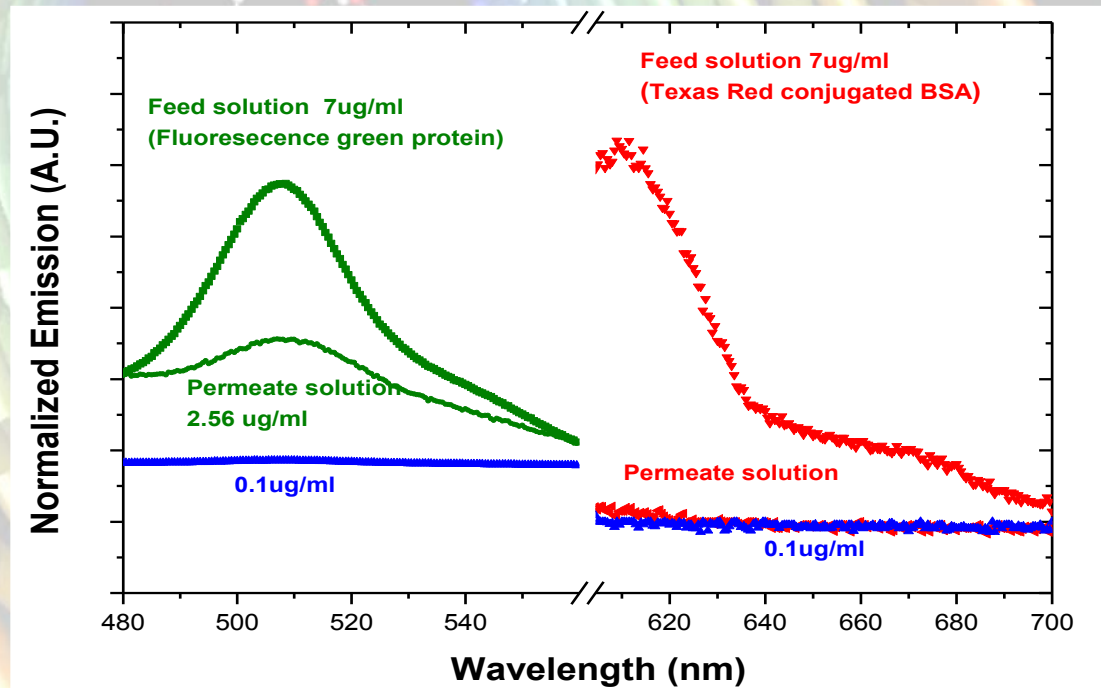
Dynamic Electrochemical Membranes for Continuous Affinity Protein Separation  
Z. Chen, T. Chen, X. Sun, B.J. Hinds  
*Adv. Funct. Mater.* 24(27) 4317-23 2014

# Pulse Electrophoretic Pumping Process



- 1. Binding cycle:** the imidazole at the feed pore is repelled and His-tagged GFP is selectively captured by the nickel receptor thereby blocking the pores as a gatekeeper.
- 2. Release and pumping cycle:** Cationic Imidazole from the permeate solution is pumped to the feed solution to release the His-tagged GFP. The anionic His-tagged GFP is selectively transported to the permeate solution by electrophoresis.

# Pulsed Electrophoretic Pumping Success in Separations

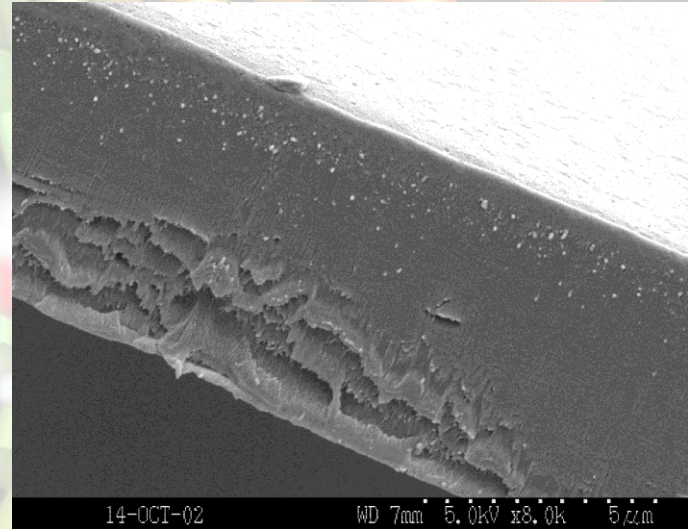
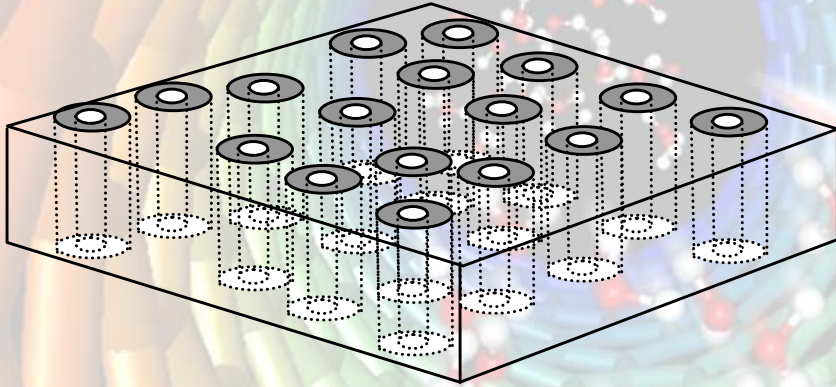


Fluorescence spectra showing the emission intensity of the feed and permeate solutions after pulse electrophoresis. The release and pumping cycle time is 14s, the binding cycle time is 1s. The concentration of imidazole in the permeate solution is 10 mM

**The trade off challenge between flux and selectivity is addressed with the pulse electrophoretic pumping. The selectivity achieved was as high as 16.**



# Conclusions



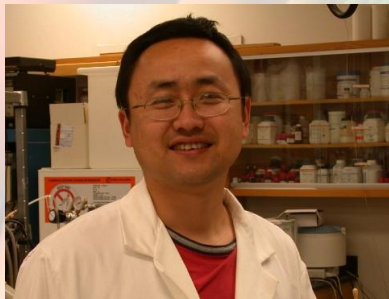
- **Membranes are an area of opportunity for reinvention**
- **CNT fluidics is remarkable but based on ‘perfection’**
- **Key to mimic nature is to pump in regions of selectivity**
- **Electro-active membranes are a hot ‘device’ area**
- **Recently able to mimic bind and pump cycle of protein transporters for biomolecular separations**

For pdf files: username: mse632 password: nanorocks

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