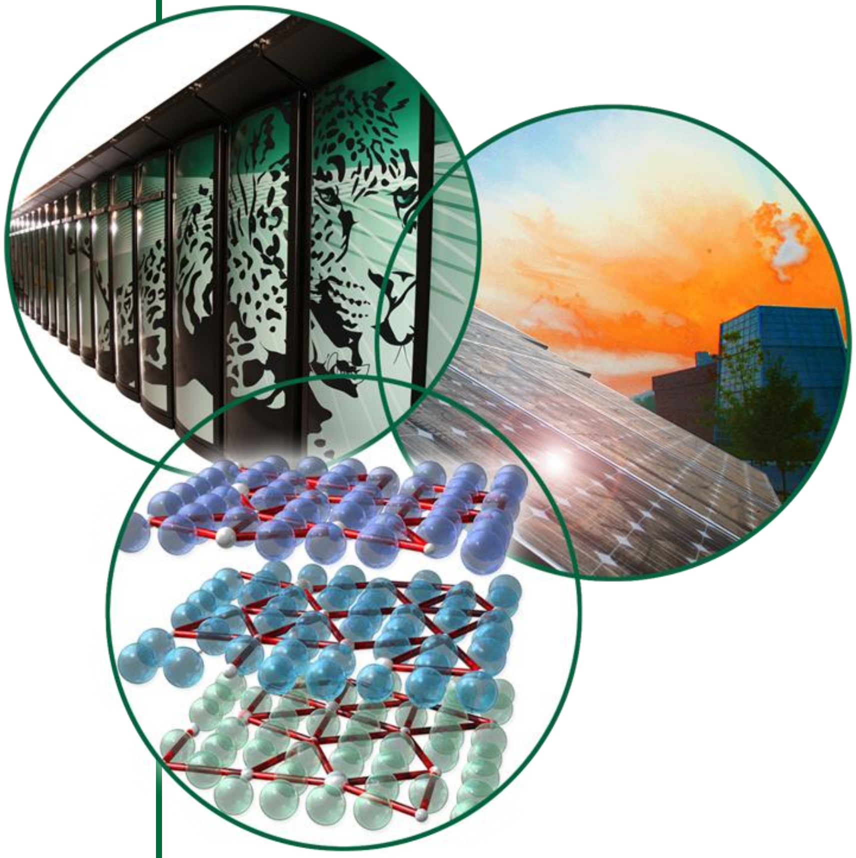
Nanofluidics and 2D Materials Based Nanosensors



Ivan Vlassiouk

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U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY

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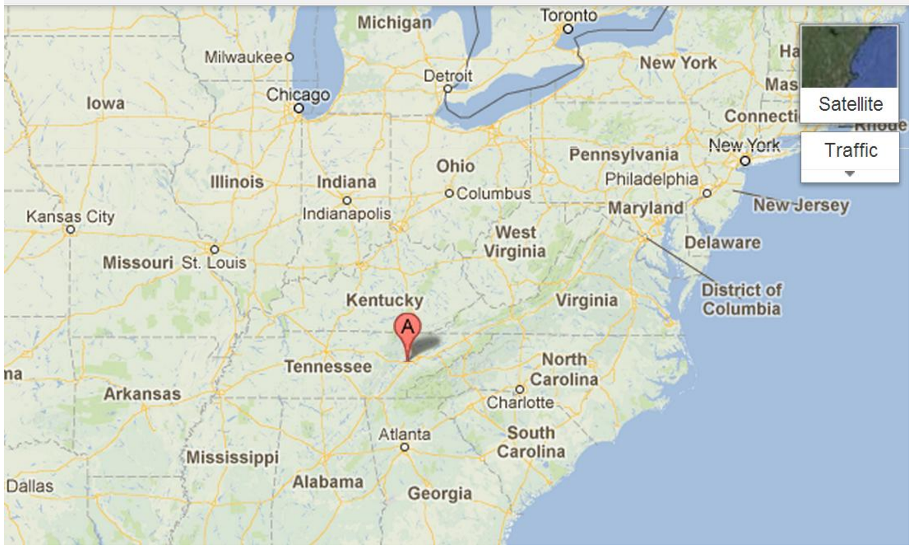
Outline

- What are nanosensors and why do we need them?
- Learning from Nature is the key!
- Microfluidics *vs* Nanofludics
- Examples of Nanosensors based on nanofluidics
- Fluidic electronics
- Graphene based membranes for sensing
- Future outlook

Oak Ridge National Laboratory



ORNL major expertise:

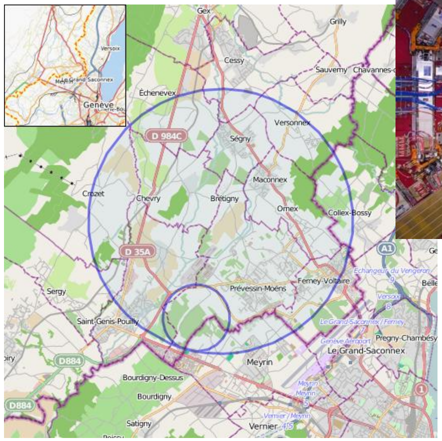
- **Engineering**
- **Material Science**
- **Supercomputing**

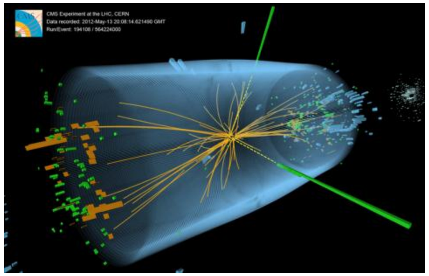
~18 petaFLOPS
Memory: 710 TB
Storage: 10 PB
Power: 8 MW

Sensors *vs* Nanosensors

- Sensors are used virtually in *every* device: from smartphones to cars and biotechnology
- We can “sense” different phenomena and objects of various scales
- From Earthquakes, Supernovas and Relic Radiation to Higgs Boson.

LHC:





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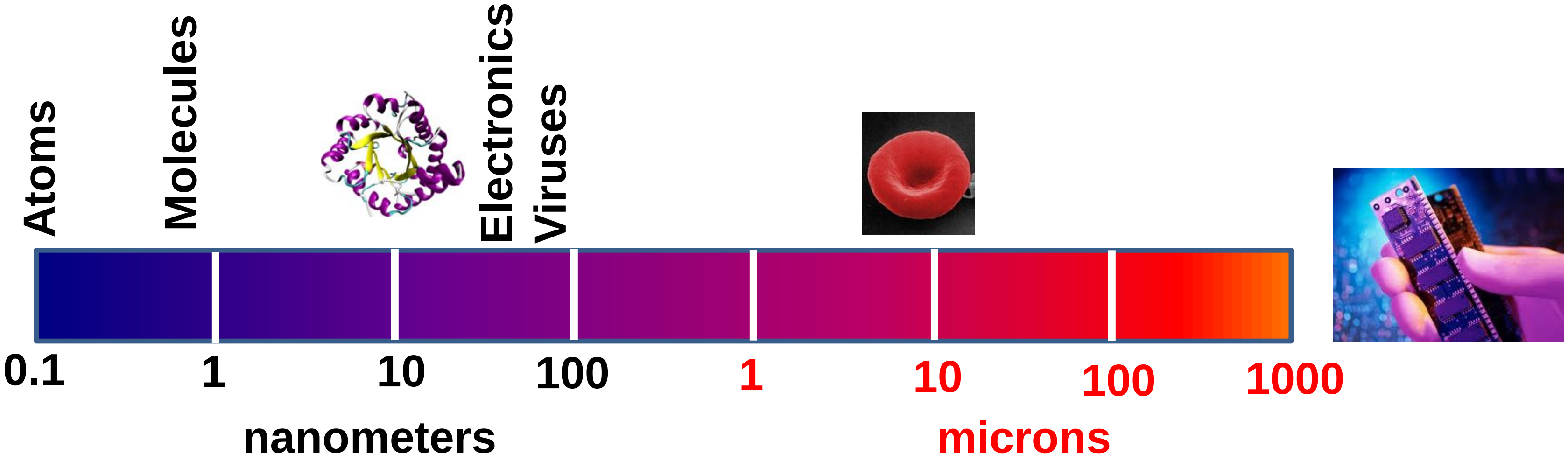
Sensors *vs* Nanosensors

Nanosensors allow for INTEGRATION of many sensing elements in small volume



Connection between nano and macro world:

- ***Neural interface: connection between living species and electronics***
- ***Artificial cells.***
- ***Bionics***

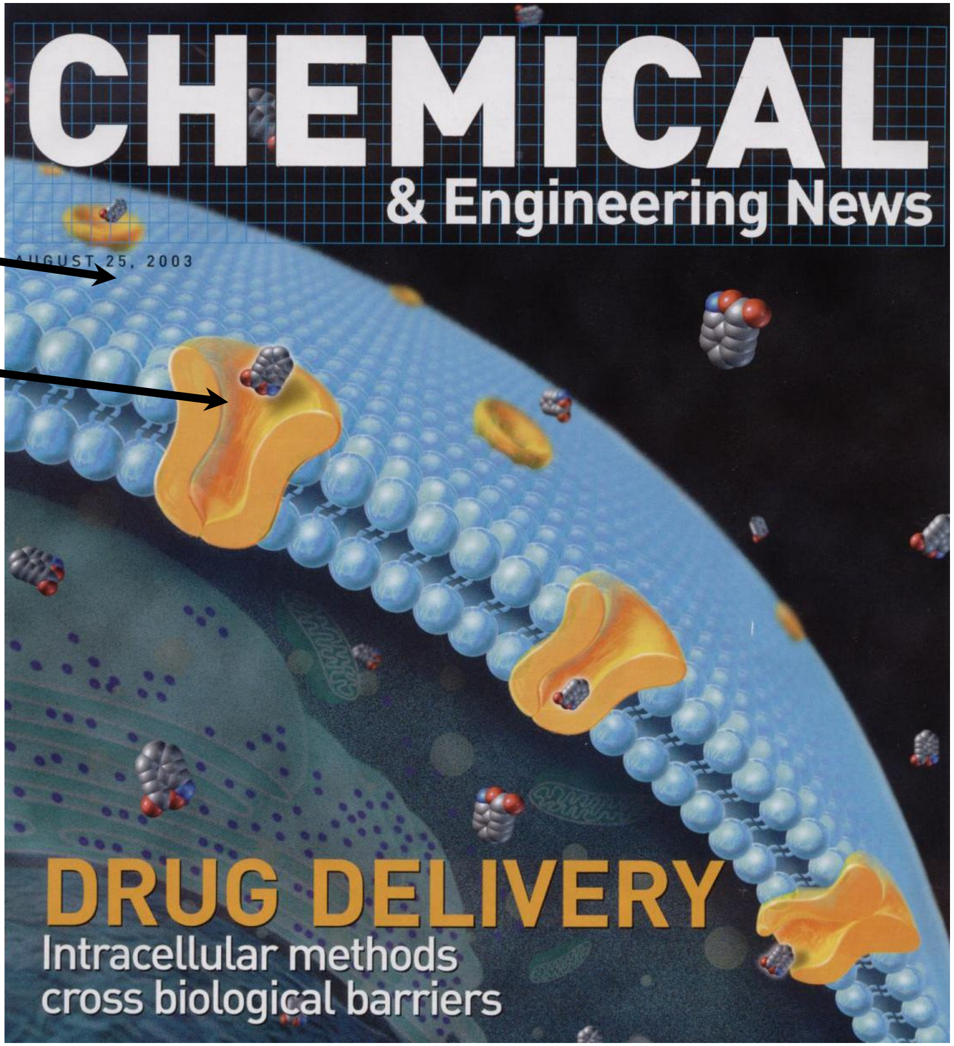
Lessons from Nature: Perfect Sensors Arrangement

Wall of a cell is an impermeable lipid (fat) membrane i.e. BARRIER

Pores in the membrane are "smart holes"

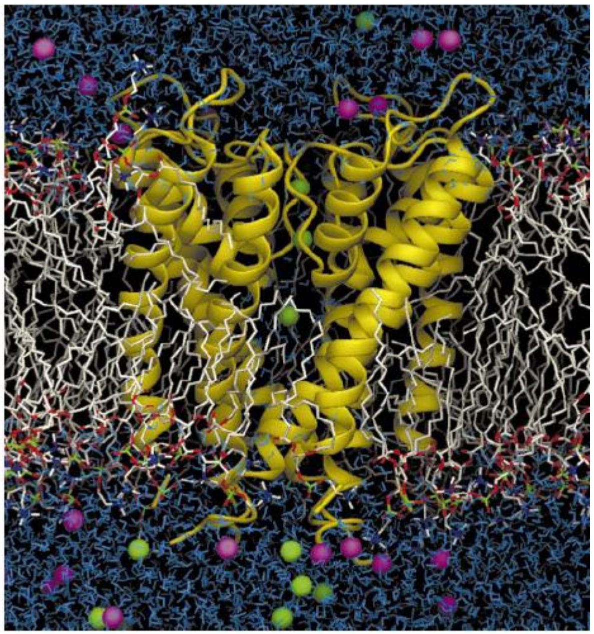
Sensitive to

- Light
- Voltage
- Chemicals
- Temperature

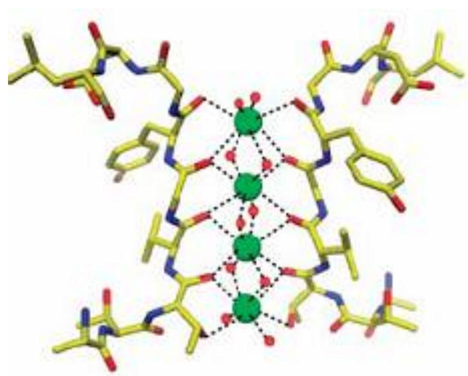


Examples of Biological Channels

A potassium selective channel is a very important player in the nerve signaling.



< 1 nm



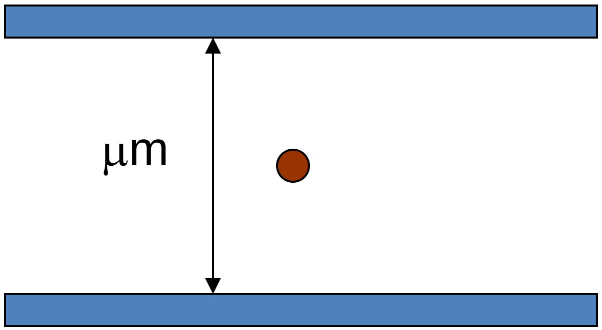
Potassium selective channel with four K^+ in the selectivity filter (right panel).

R. MacKinnon, P. Agre 2003

E. Gouaux, R. MacKinnon, *Science* **310**, 1461 (2005).
S. Berneche, B.Roux, *Nature 414,* 73 (2001).

What the Nanofluidics is?

In a macro channel ions can not interact with the channel wall significantly



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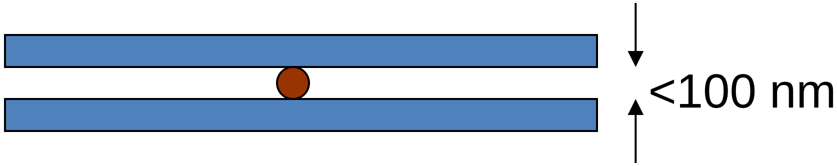
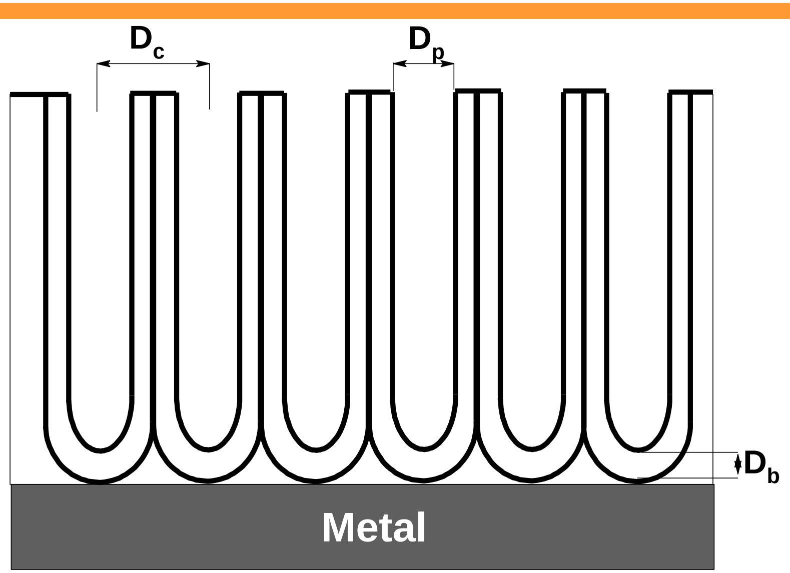
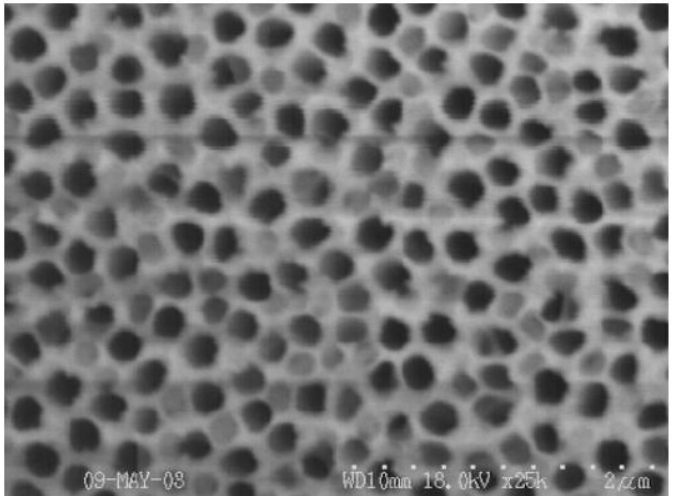
If the size of the channel is small, ions can interact with the surface!!

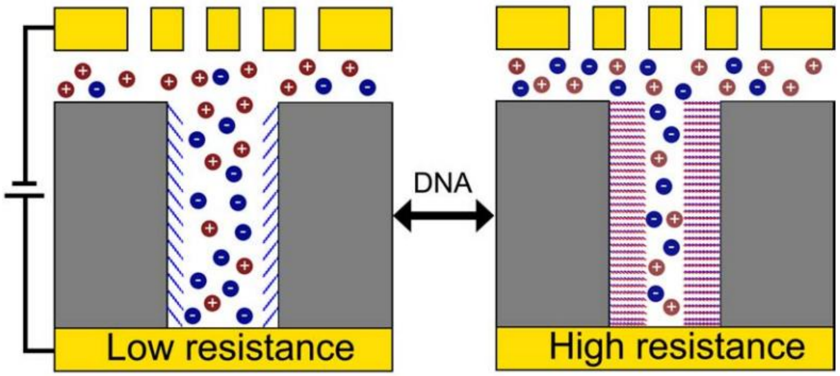


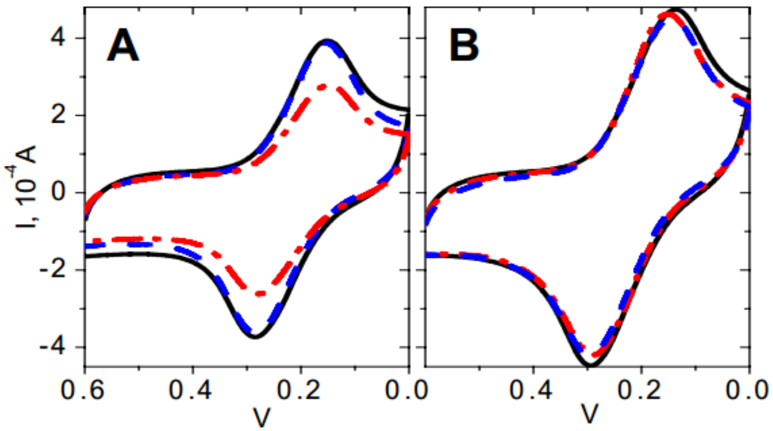
- Size of the channel
- Surface energy
- Surface Charge
- Chemical modification
- Electrostatic forces

Volume exclusion – DNA sensor and purification





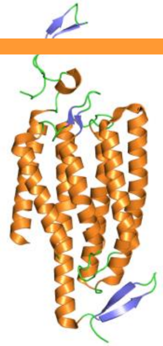




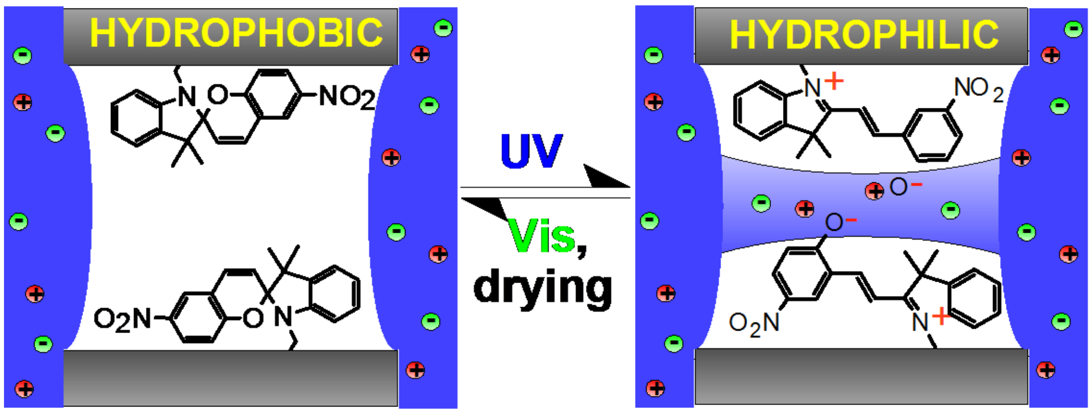
Vlassiouk et al. Langmuir, 20, 9913; Vlassiouk et al, 21, 4776

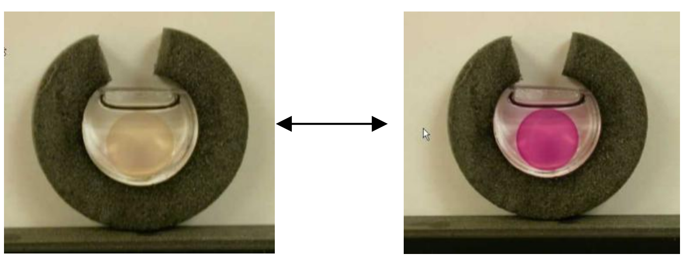
Light sensitive channels

Nature example - Channelrhodopsin

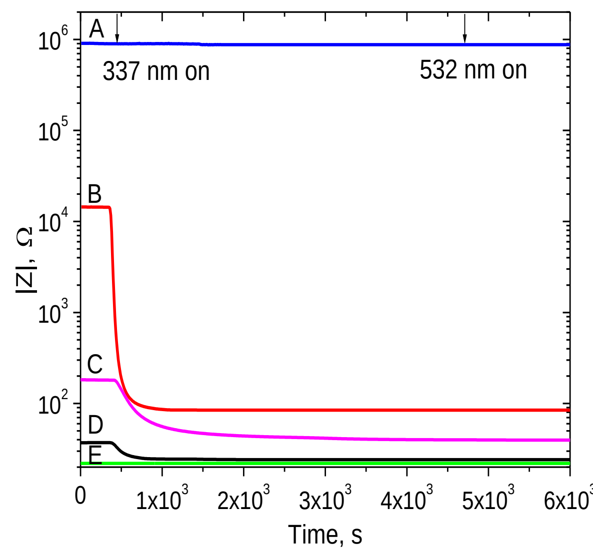


We employ hydrophobic interactions!





Resistance drops after UV irradiation

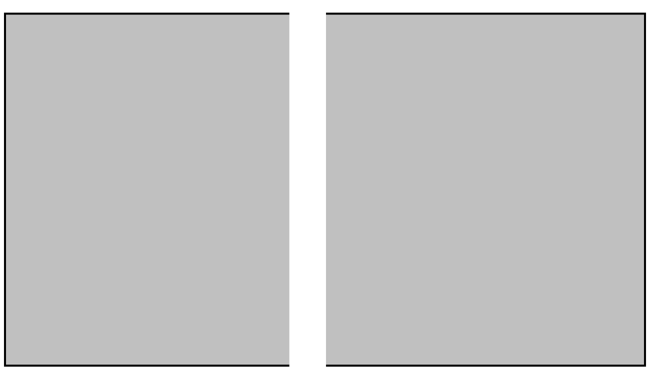


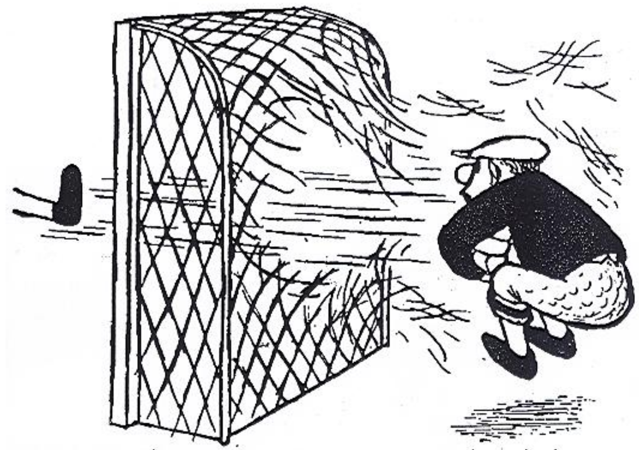
Vlassiouk et al, Nanolett, 2006, 1013-1017

Old technique for new applications: preparation of ion channel

1. Irradiation with e.g. Xe, Au, U

2. Chemical etching





E. Loriot

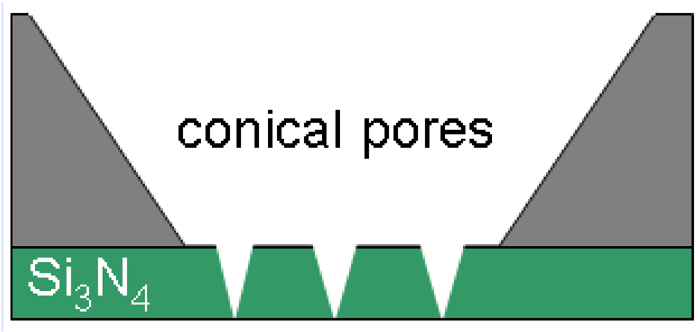
Darmstadt, Germany

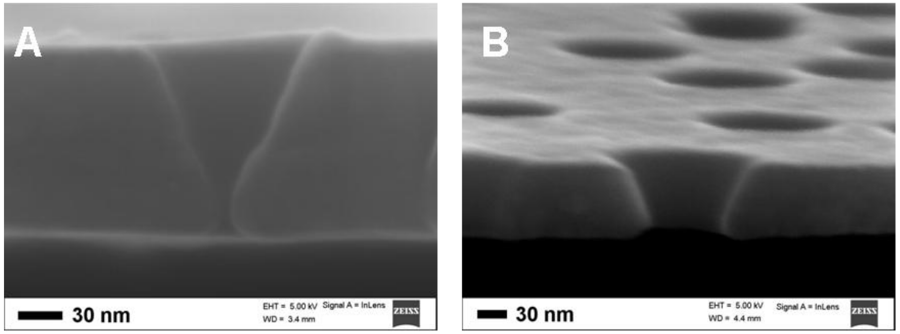
Dubna, Russia

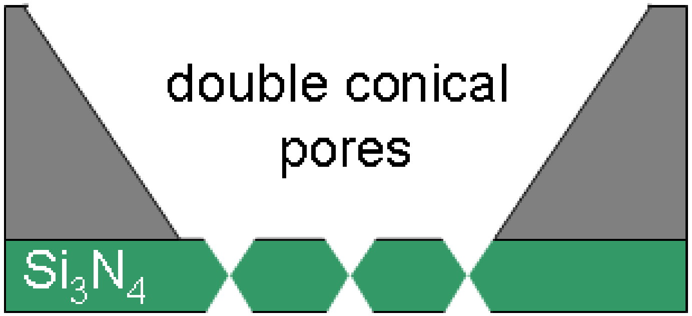
1 ion → 1 latent track → 1 pore !

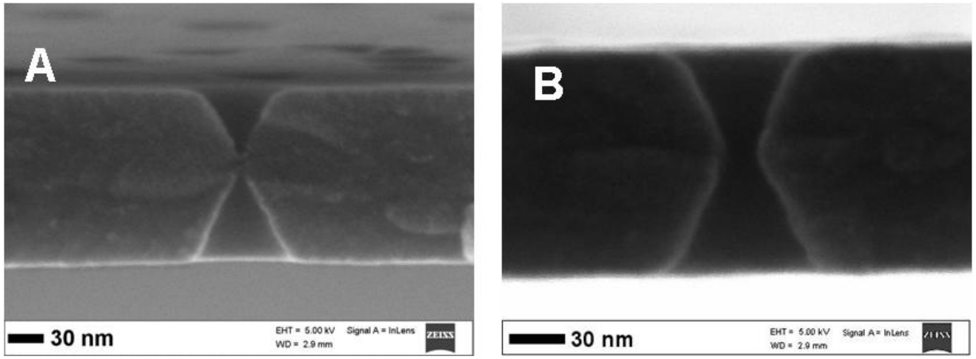
R.L. Fleischer, P.B. Price, R.M. Walker (1975)

Fabrication of nanopores array in SiN





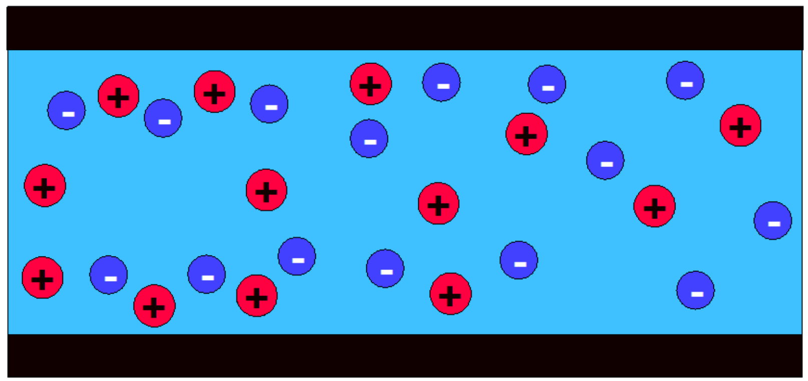




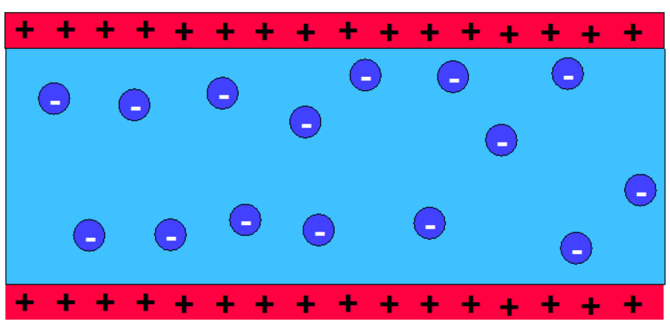
Vlassiouk et al, PNAS, 2009, 106, 21039

Electrostatics – paramount for nanofluidics based nanosensors.

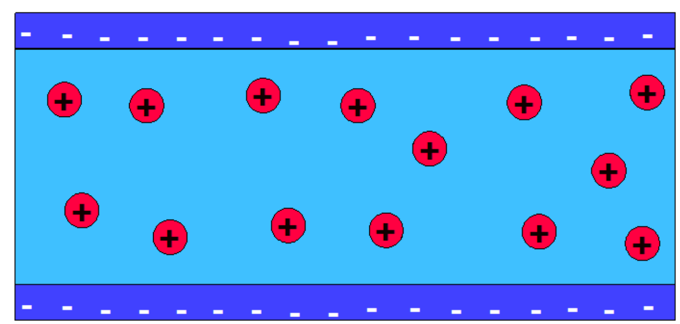
Microchannels – concentrations of positive and negative ions are equal.



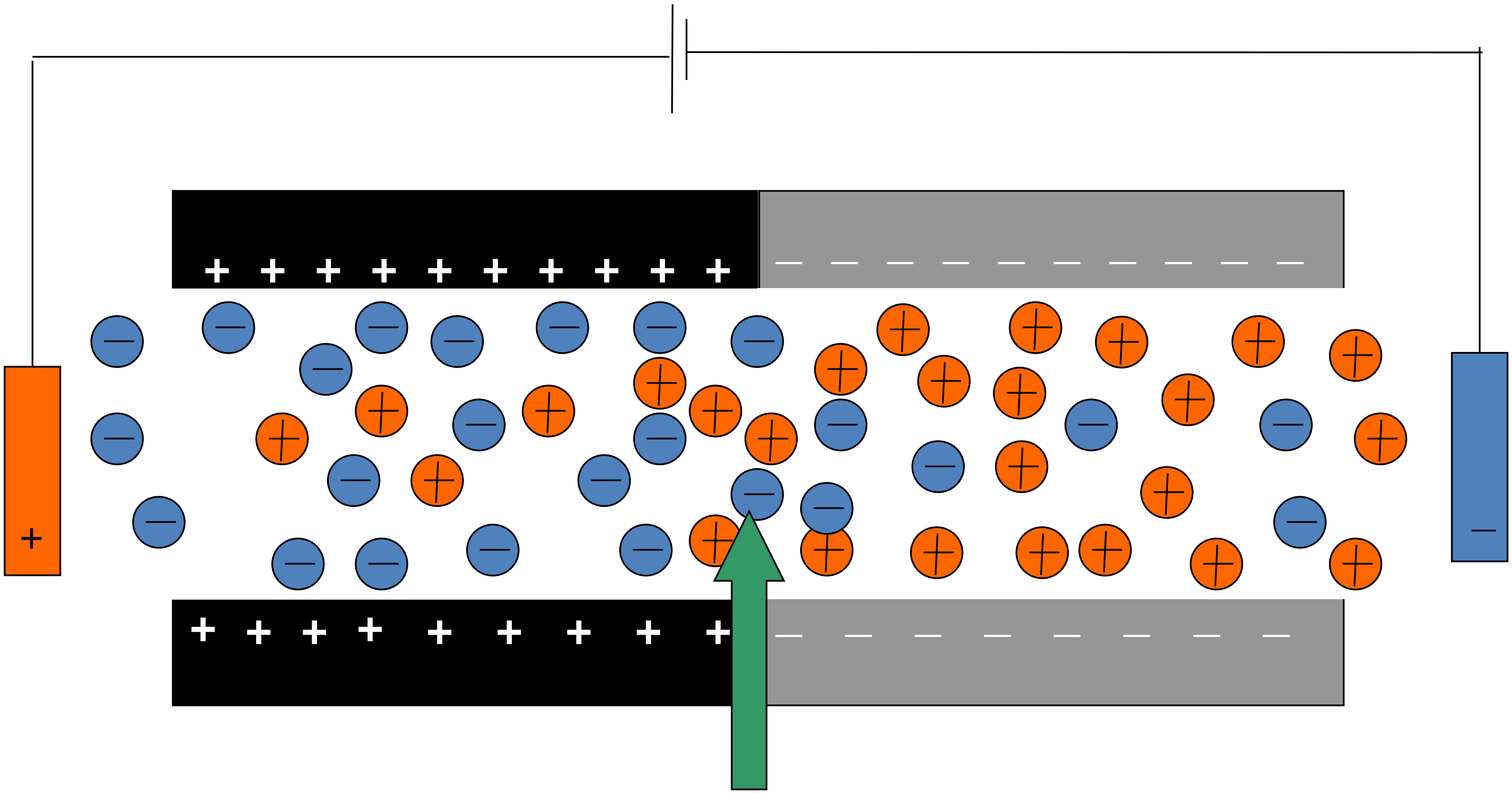
Nanochannels – small volume but large surface:
concentration of counter ions is higher!



$$\Delta C = \frac{2\sigma}{er}$$



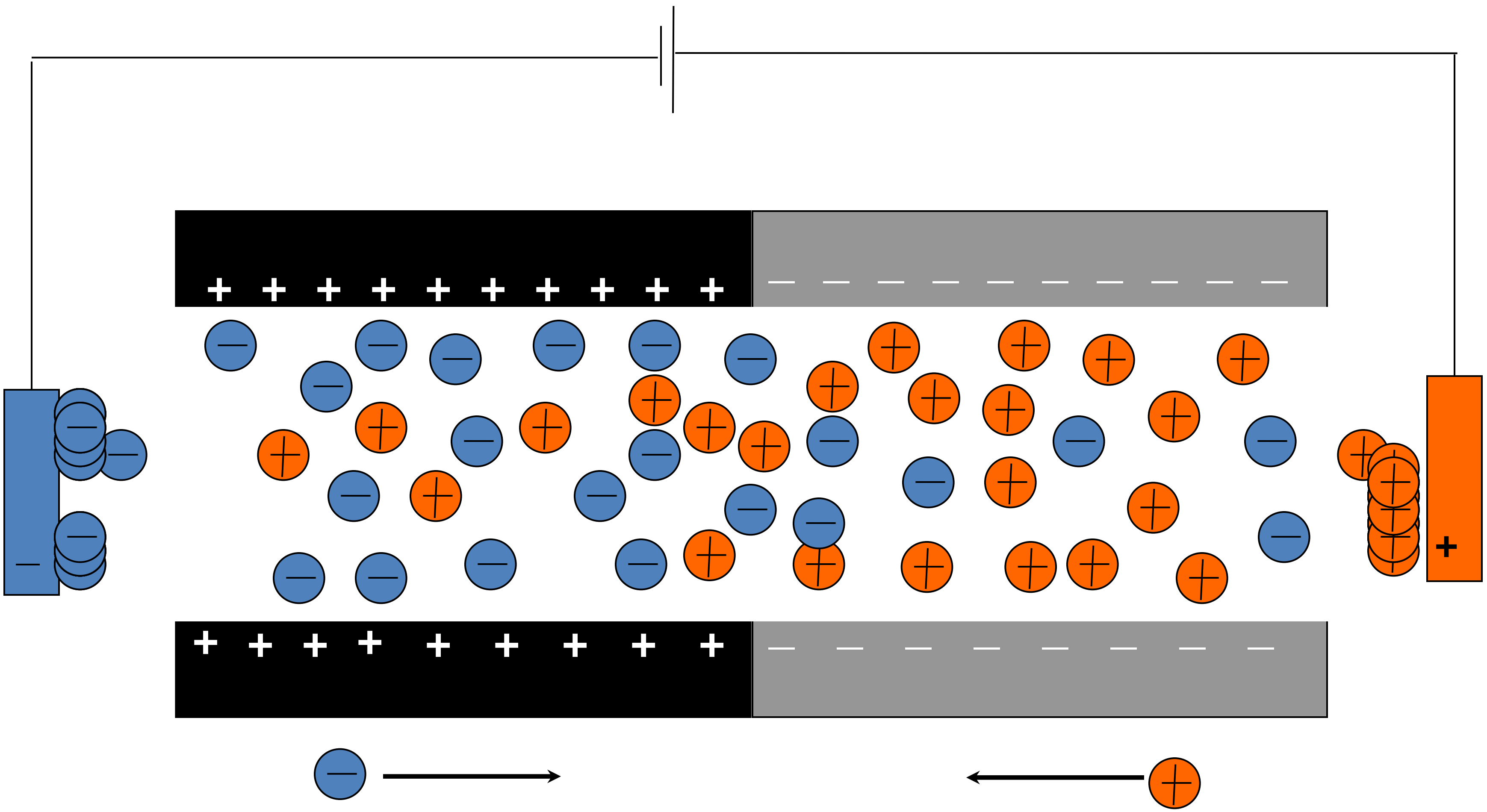
How to Make an Ionic diode?



I. Vlassiouk, Z.S. Siwy, *Nano Lett.* **7**, 553 (2007)

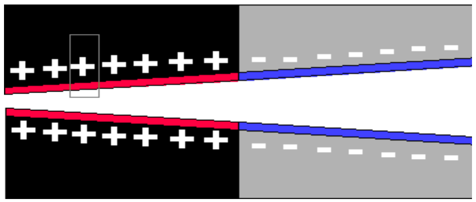
H. Daiguji, P. Yang, A. Majumdar, *NanoLett.*, **4**, 137 (2005).

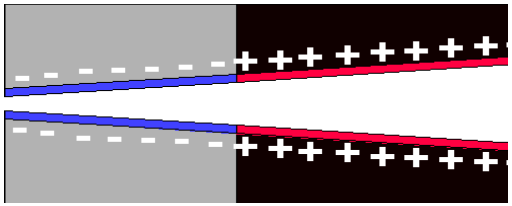
OPEN State of Ionic Diode.



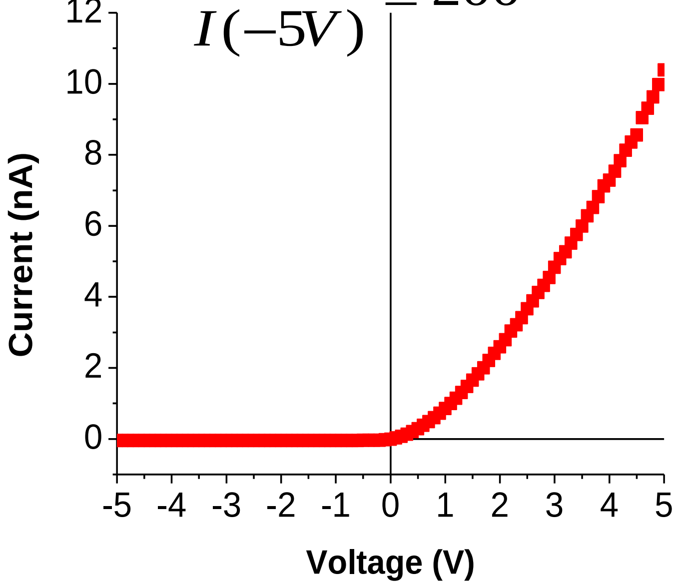
BIPOLAR DEVICE – current carried by both

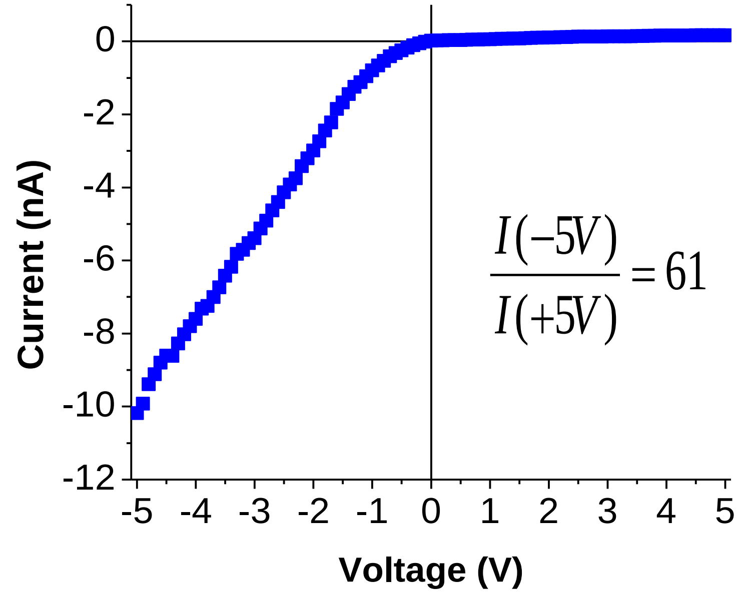
Ionic Bipolar Diodes





$$\frac{I(+5V)}{I(-5V)} \cong 200$$



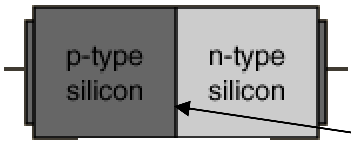


$$\frac{I(-5V)}{I(+5V)} = 61$$

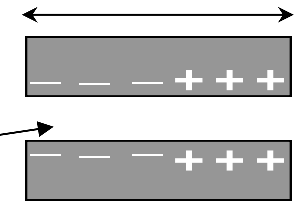
5 nm pore

I. Vlassiouk, Z.S. Siwy, *Nano Lett.* **7**, 553 (2007);

1D Analytical solution



Depletion zone



$$l_{n,p} \approx \sqrt{\frac{\left(\frac{N_a}{N_d}\right)^{-1} \varepsilon\varepsilon_0 \Delta V}{(N_d + N_a)2\pi e}}$$

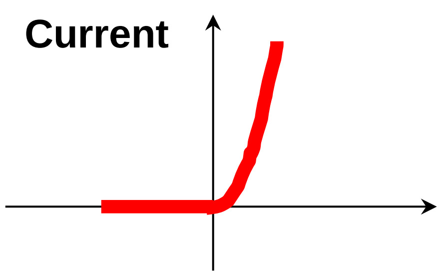
doping

$$l_{dep} \approx \sqrt{\frac{\Delta V a \varepsilon\varepsilon_0}{\sigma}}$$

***a* – pore radius**

σ - surface charge density

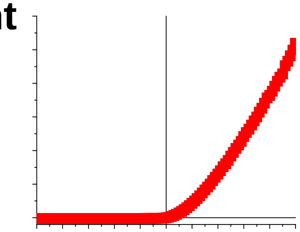
$$I_{open} = \left(I_h^{gen} + I_e^{gen}\right)\left(e^{\frac{eV}{k_B T}} - 1\right)$$



$$I_{closed} = \left(I_h^{gen} + I_e^{gen}\right)$$

N.W. Ashcroft, N.D. Mermin, *Solid State Physics*, Thomas Learning, 1976

$$I_{open}^{BP} \approx \left(\frac{ea}{2k_B T}\right)^2 \frac{e\pi D \Delta C}{L}(V + V_o)^2$$

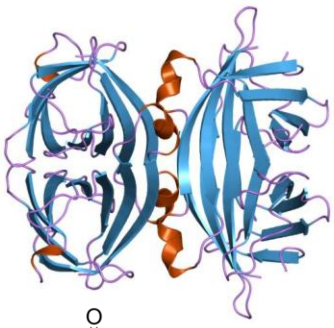


$$I_{closed}^{BP} = 2e^2 \pi D \frac{a^3 C_{bulk}^2}{\sigma L}$$

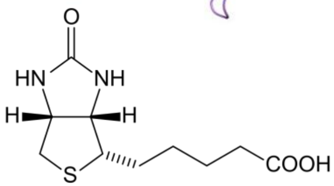
I. Vlassiouk, S. Smirnov, Z. Siwy, *ACS Nano* **2**, 1589 (2008)

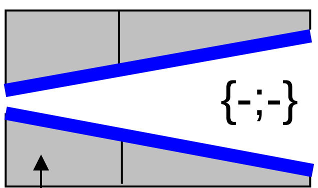
Biosensing with Nanofluidic Diodes.

Avidin



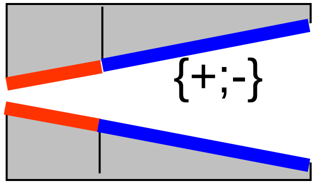
Biotin

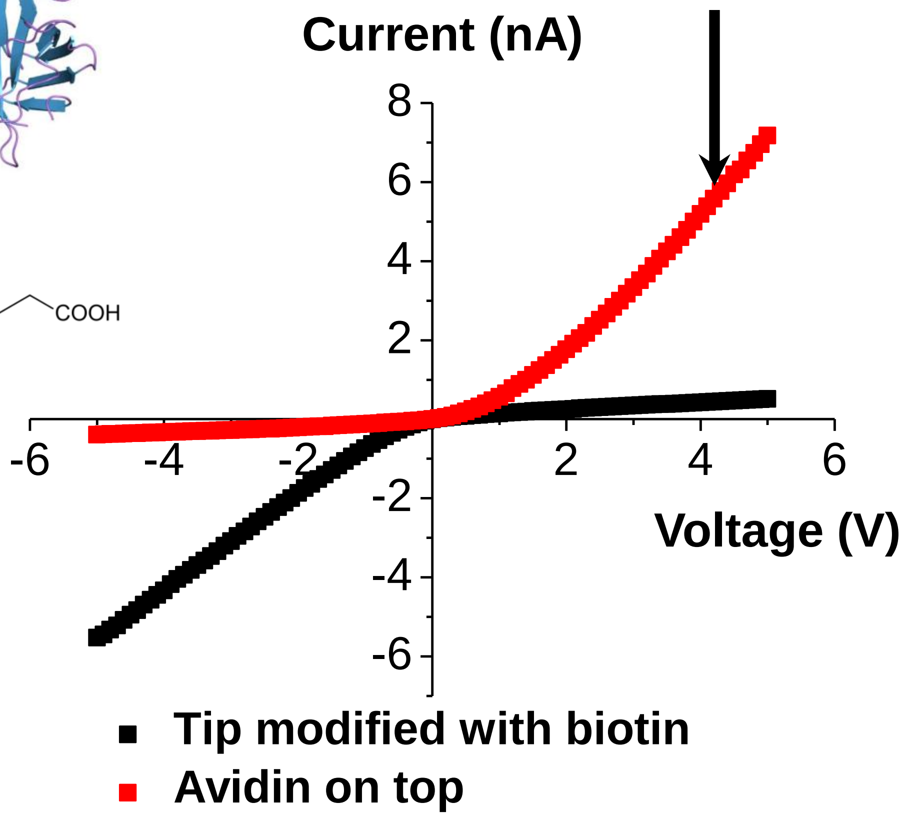




biotin

Biotin - Avidin

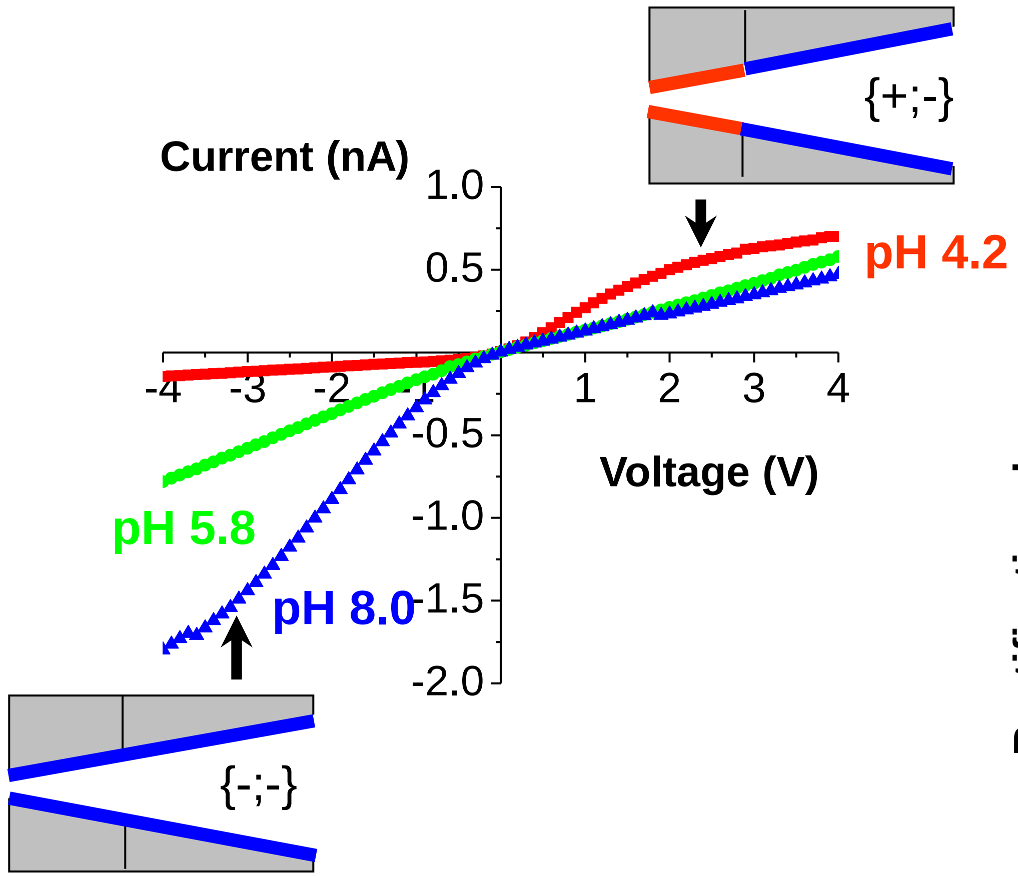


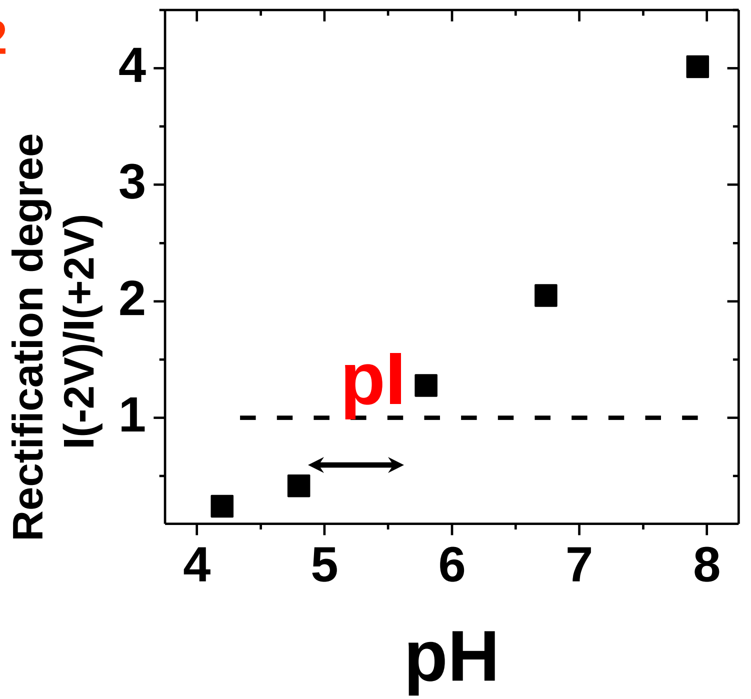


Avidin is positive!

Vlassiouk et al, JACS, 2009, 131, 8211

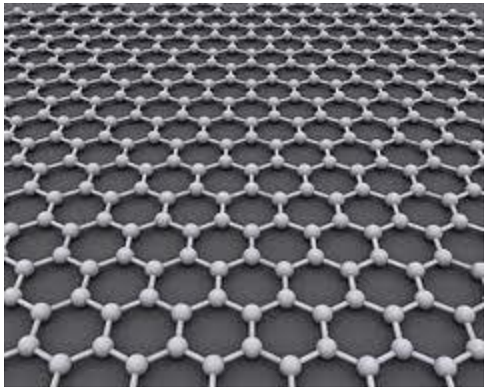
Biosensing with Nanofluidic Diodes. Streptavidin. pH meter.





Vlassiouk et al, JACS, 2009, 131, 8211

Graphene – atomically thin layer of carbon

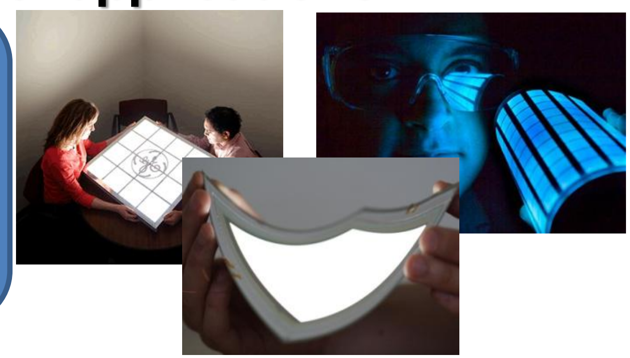


- Transparent
- Flexible
- High Electrical conductivity
- High Thermal Conductivity
- Exceptional Mechanical Strength

Unique properties define wide range of applications:

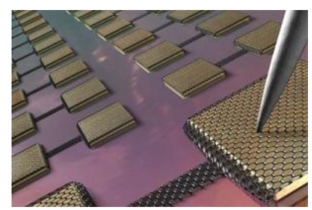
Applications Area 1
Transparent conductor:

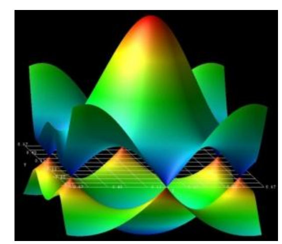
- Touch Screens
- Solar Cells
- Solid State Lighting
- Smart Windows
- LCD Displays



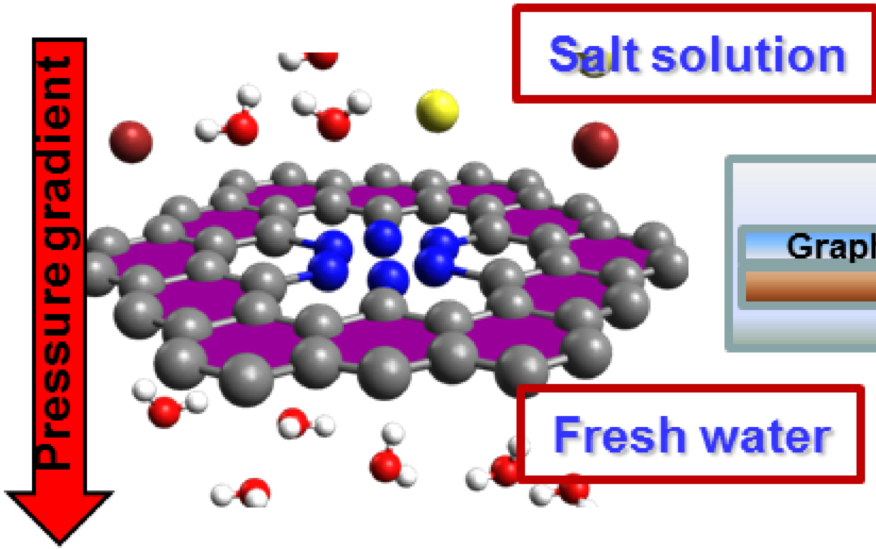
Applications Area 2
Active component:

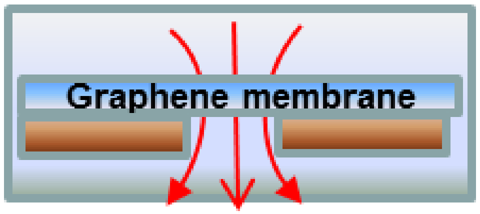
- Electronics
- Optoelectronics
- RF devices
- Communication
- Sensing





Graphene: Perfect membrane?

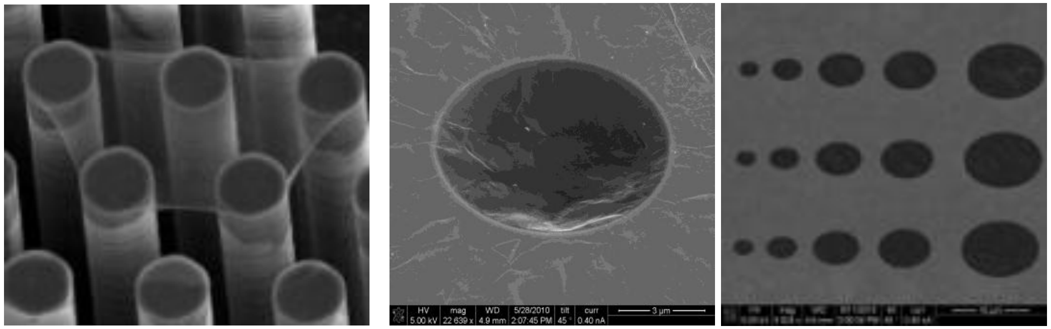




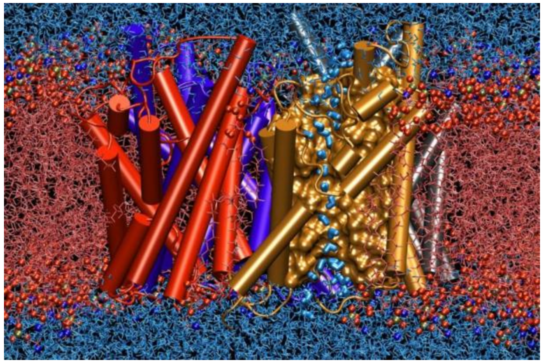
Perfect for

- **Desalination**
- **Separation**

Graphene suspended structure fabrication:

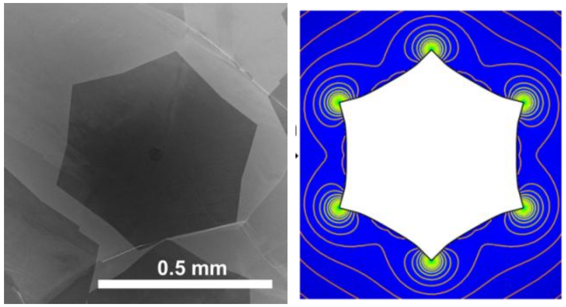


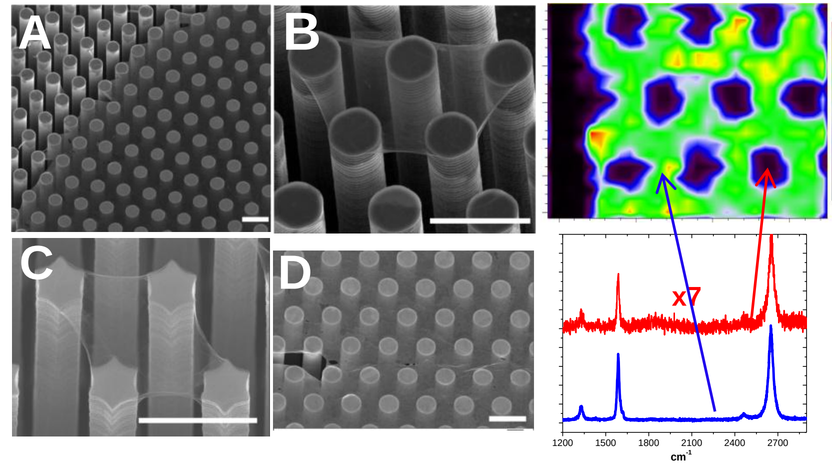
Aquaporin:



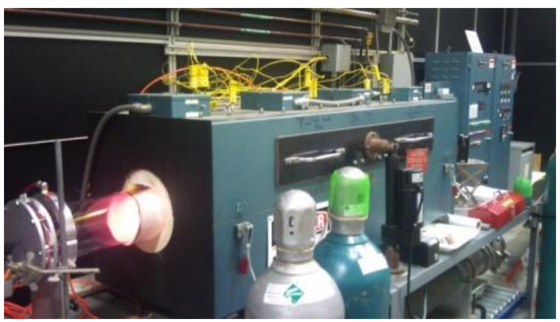
Good quality, Large Quantity

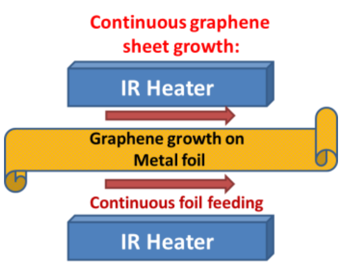
1 mm crystals

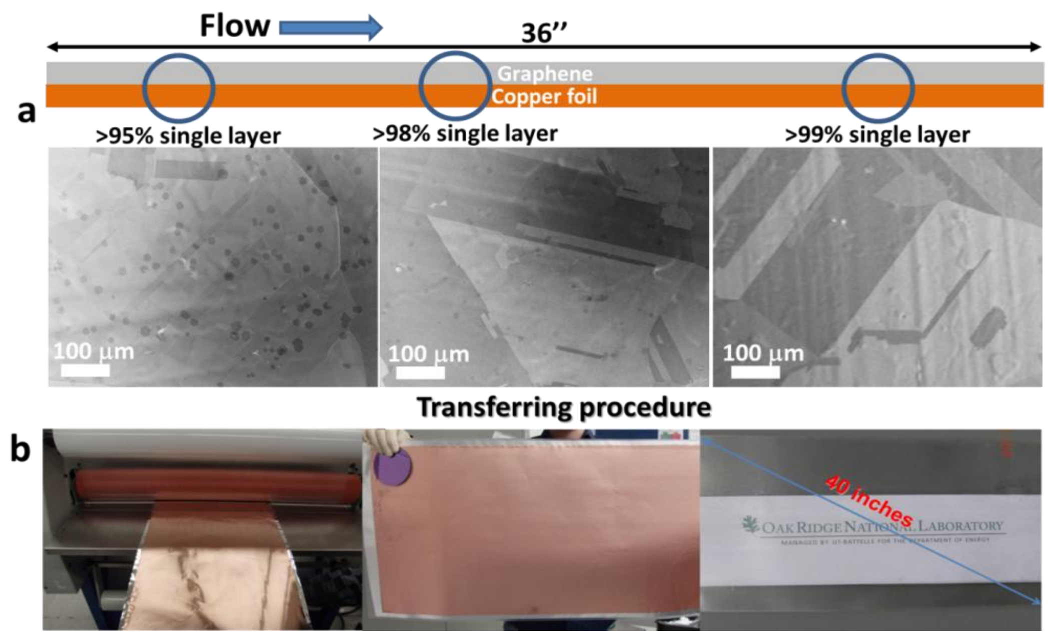




40'' continues film







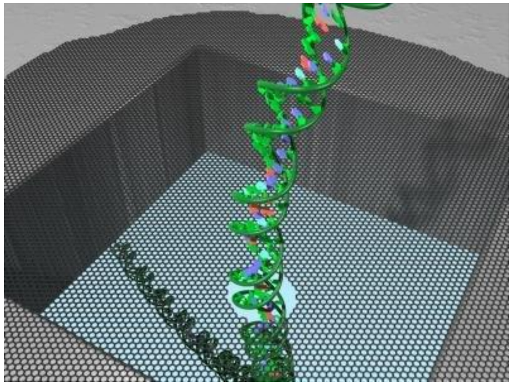
Vlassiouk et al, Nanotechnology, **2011**, 22, 275716; Vlassiouk et al, ACS Nano, **2011**, 5, 6069; Vlassiouk et al, Carbon, **2013**, 54, 58; Vlassiouk et al, J. Phys. Chem. C, **2013**, 117, 18919

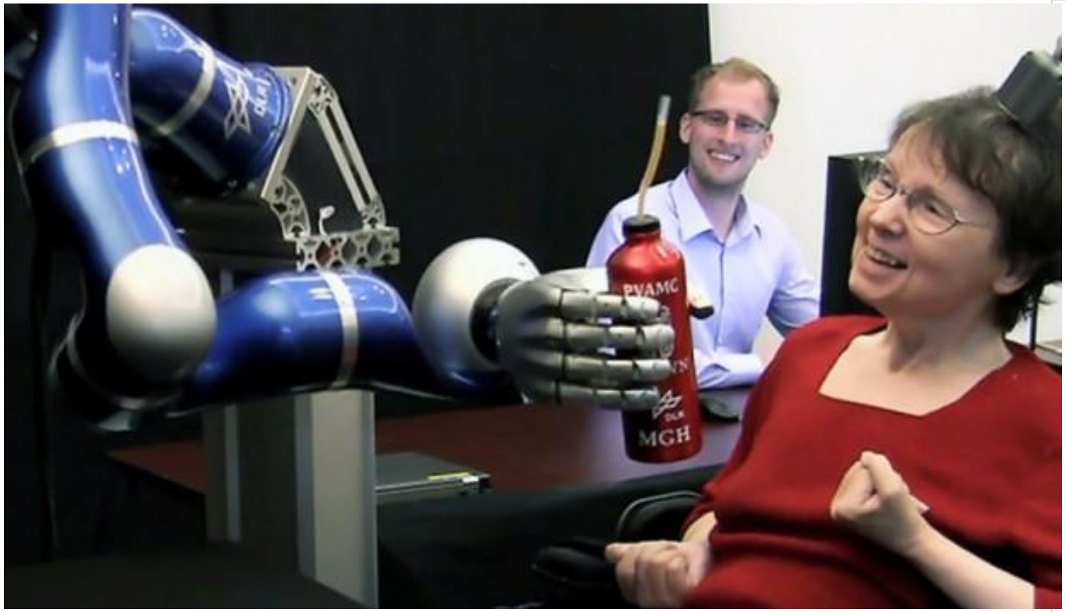
Future outlook

- **Personalized medicine**

- **Bionics / mimicking the Nature**

- **Neural interface**





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