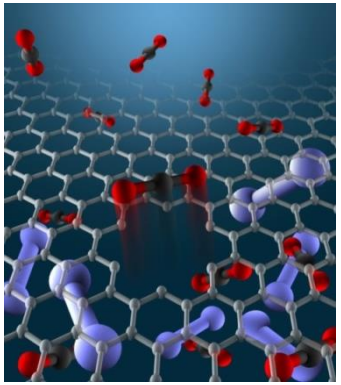
BOSTON UNIVERSITY

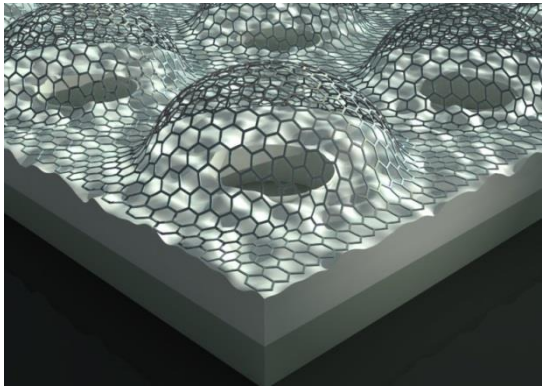
Atomic and Molecular Separation through Porous Graphene

Lauren Cantley
David Lloyd
Guang Yang
Isabela Haghighi
Nigel Rodriguez
Ian Herd
Scott Bunch

Xinghui Liu
Luda Wang
Steven Koenig
Eric Koch
Emily Misnick
Mariah Szpunar
Miguel Rodriguez
Phi Pham
Peter Musso
Michael Tanksalvala
Tony Zhou
Guillermo Acosta
Lauren Cosgriff

Collaborators:
Narasimha Boddeti
Rong Long
Jianliang Xiao
Martin Dunn
John Pellegrino
Michael Strano
Lee Drahushuk
Pinshane Huang
Jon Travis
Andrew Cavanaugh
Steve George
Jiwon Suk
Jason Gray
Harris Hall
Victor Bright
Charles Rogers
Rod Ruoff





Department of Mechanical Engineering

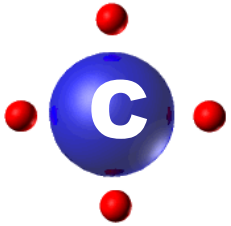
Division of Materials Science and Engineering

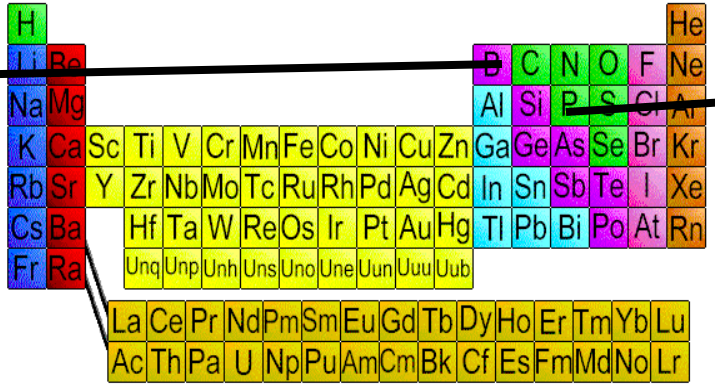
Department of Physics (courtesy)

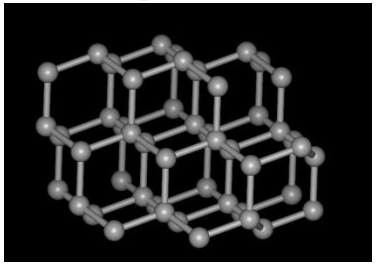
Support:

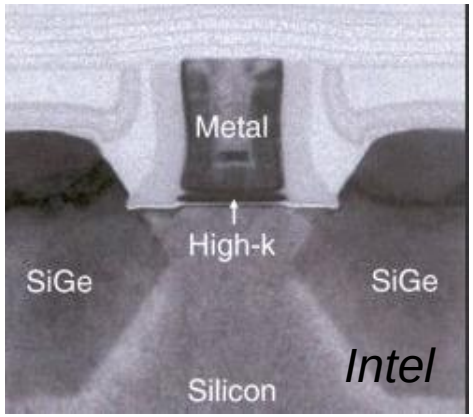
NSF, DARPA, CU, BU

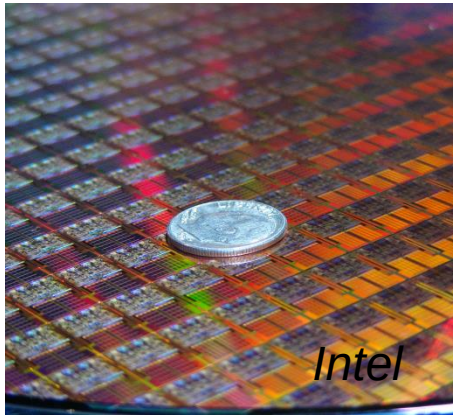
Carbon vs. Silicon

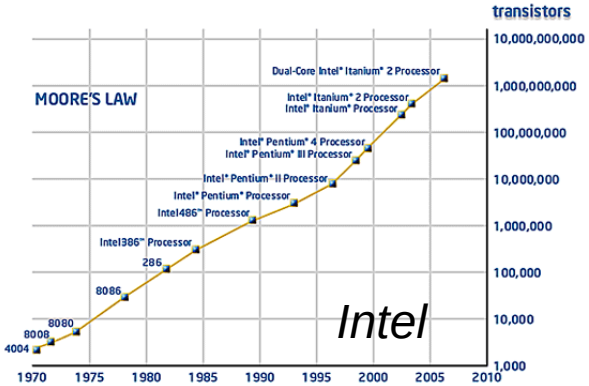






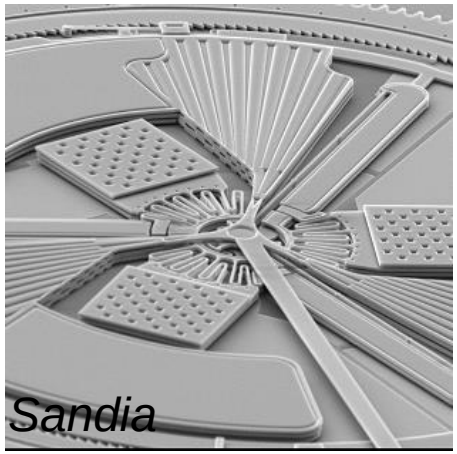






Electrical

~ $1 Trillion business



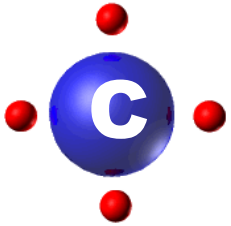
1. Accelerometers
2. Pressure Sensors
3. Ink Jet Printer Nozzles
4. Displays
5. RF MEMS

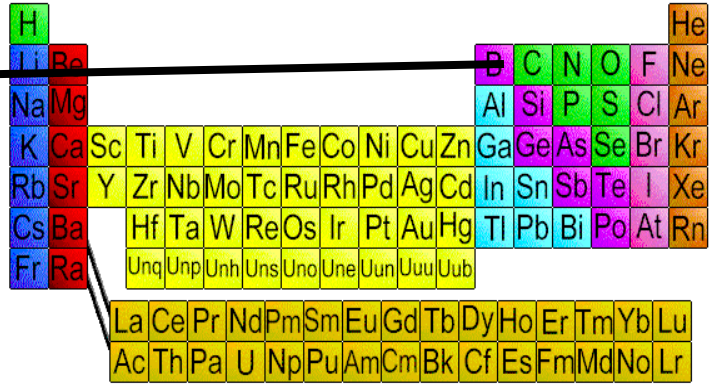
Mechanical

$12 Billion business

12% annual growth

Carbon vs. Silicon





Superior Properties

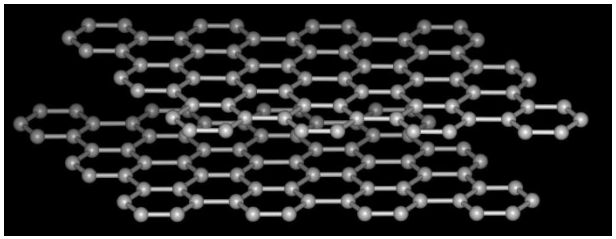
Electrical

Mechanical

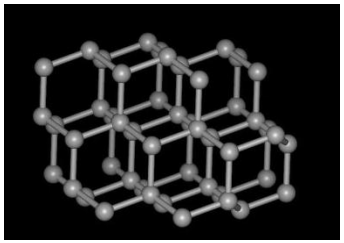
Thermal

Different Bonding

Graphite

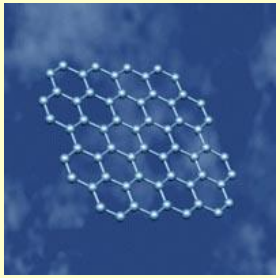


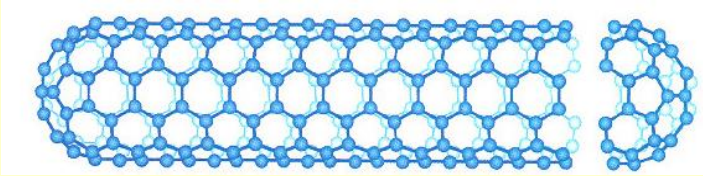
Diamond



Apollo Diamonds

Graphene/Nanotubes





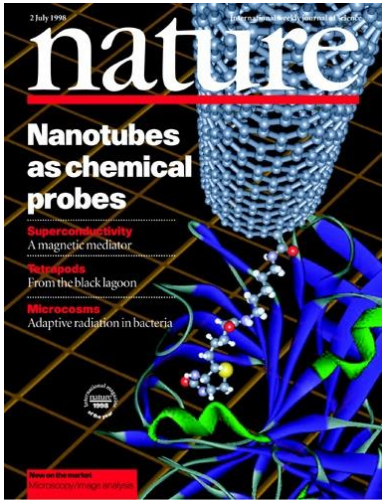
Nanotubes

1997

Electrical

1997

Mechanical



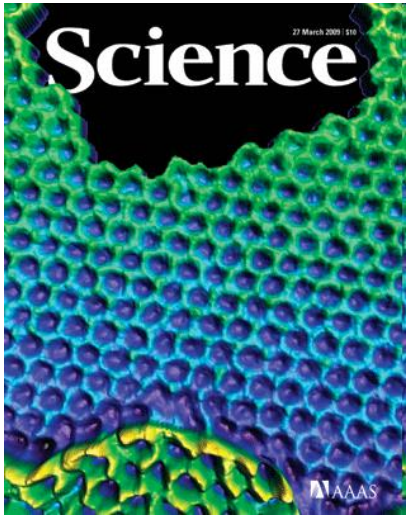
1998

Chemical/Biological

Graphene

2006

Electrical



2009

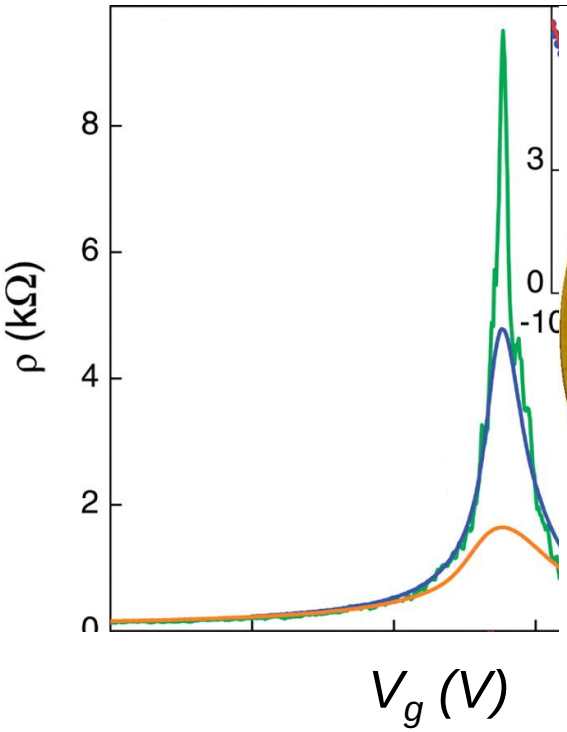
Mechanical

2010

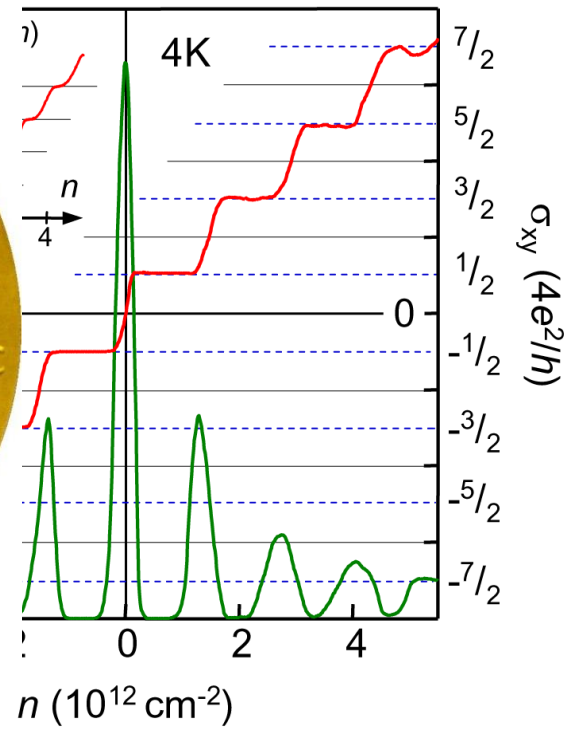
Chemical/Biological

Graphene (Electrical)

Manchester (Novoselov, Geim, et al.)



Manchester (Novoselov, Geim, et al.)



2010 Physics

Novoselov and Geim

Gate Dependent Transport

Novoselov et al. Science (2004)

Integer Quantum Hall Effect

Novoselov et al. Nature (2005)

(Columbia) Zhang et al. Nature (2005)

What about the Mechanical Properties?

Graphene Mechanics

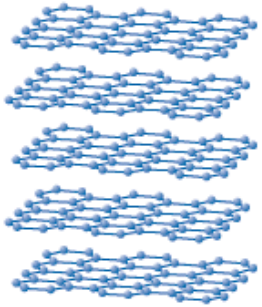
Adhesion – Extremely Flexible Membrane

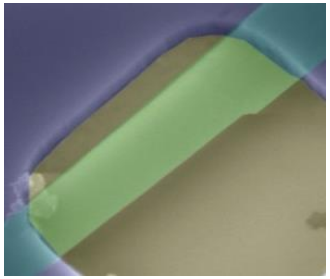
vdw forces holds sheets together

Adhesion clamps sample to substrate

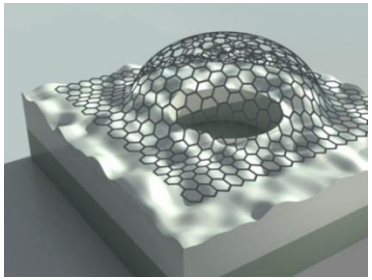
Mechanics and electronics influence by substrate

Strain and flexibility dictated by adhesion

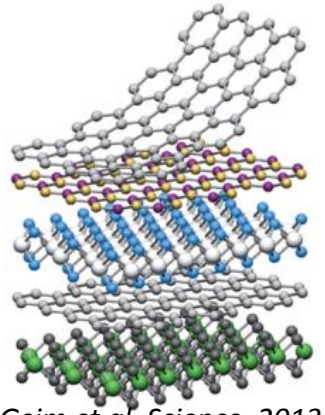




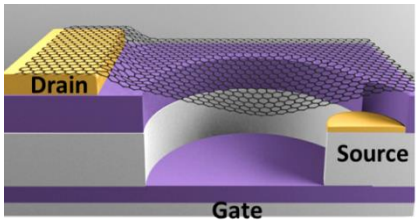
J. S. Bunch et.al. Science ***315,*** *490-3 (2007)*



S.P. Koenig et al., Nature Nanotechnology, **6**, 543–546 (2011)



Geim et al. Science, 2013



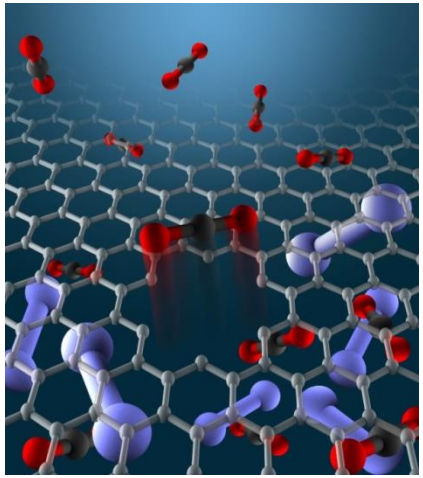
Xinghui Liu et al. Advanced Materials ***26,*** *1571-1576 (2014)*

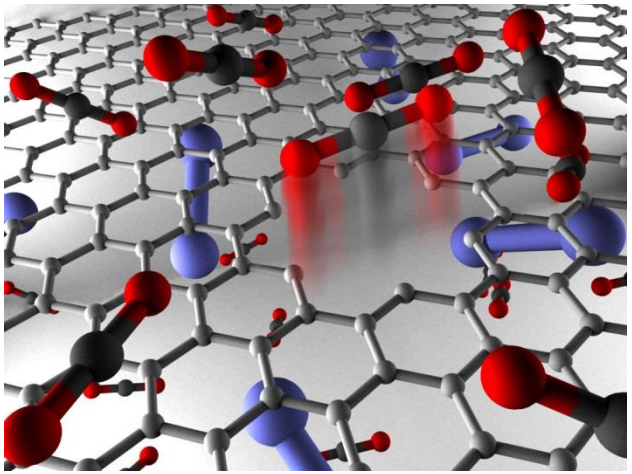
wikipedia

Molecular Separation

Thin membrane

Well defined pores

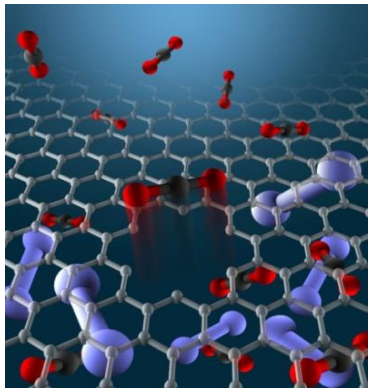




S.P. Koenig et al., Nature Nanotechnology, **7**, 728-732 (2012)

Graphene as a Membrane

Gas Separation: control what molecules pass



Koenig S.P., Wang L. et al., Nature Nanotechnology, **7**, 728-732 (2012)

ORNL

D. Jiang, V.R. Cooper, and S. Dai *Nano Lett.* **9**, 4019-4024 (2009).

Karnik Group (MIT) - CVD

ACS Nano, **6**, 10130-10138 (2012).

Hobum Park Group (Korea)

Kim et al, *Science* **342**, 91-95 (2013).

Miao Yu (Univ South Carolina)

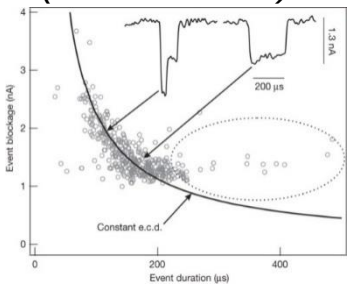
Li et al, *Science* **342**, 95-98 (2013).

Hyung Gyu Park (ETH Zurich)

Celebi et al, *Science* **344**, 289-292 (2014).

DNA Sequencing

Golovchenko Group (Harvard Univ.)



Garaj S. et al. Nature **467**, 190 (2010)

Drndić Group (Univ. of Pennsylvania)

Merchant C. et al.

Nano Lett., **2010**, *10* (8), pp 2915–2921

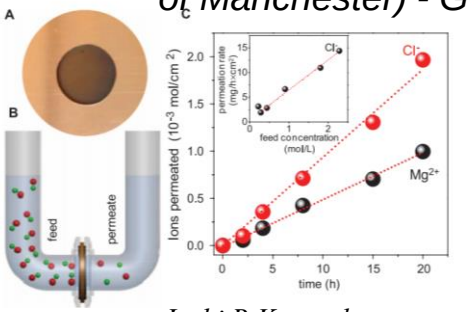
Dekker Group (TU Delft)

Schneider G. et al.

Nano Lett., **2010**, *10* (8), pp 3163–3167

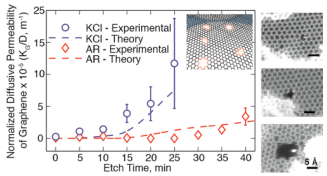
Liquid-phase Filtration/ Desalination

GeimGroup (Univ. of Manchester) - GO



Joshi R.K. et al.
Science **343**, 752-754 (2014)

Karnik Group (MIT) - CVD



O'Hern S., et al.

Nano Lett., **2014**, *14* (3), pp 1234–1241

ORNL

Surwarde., et al.

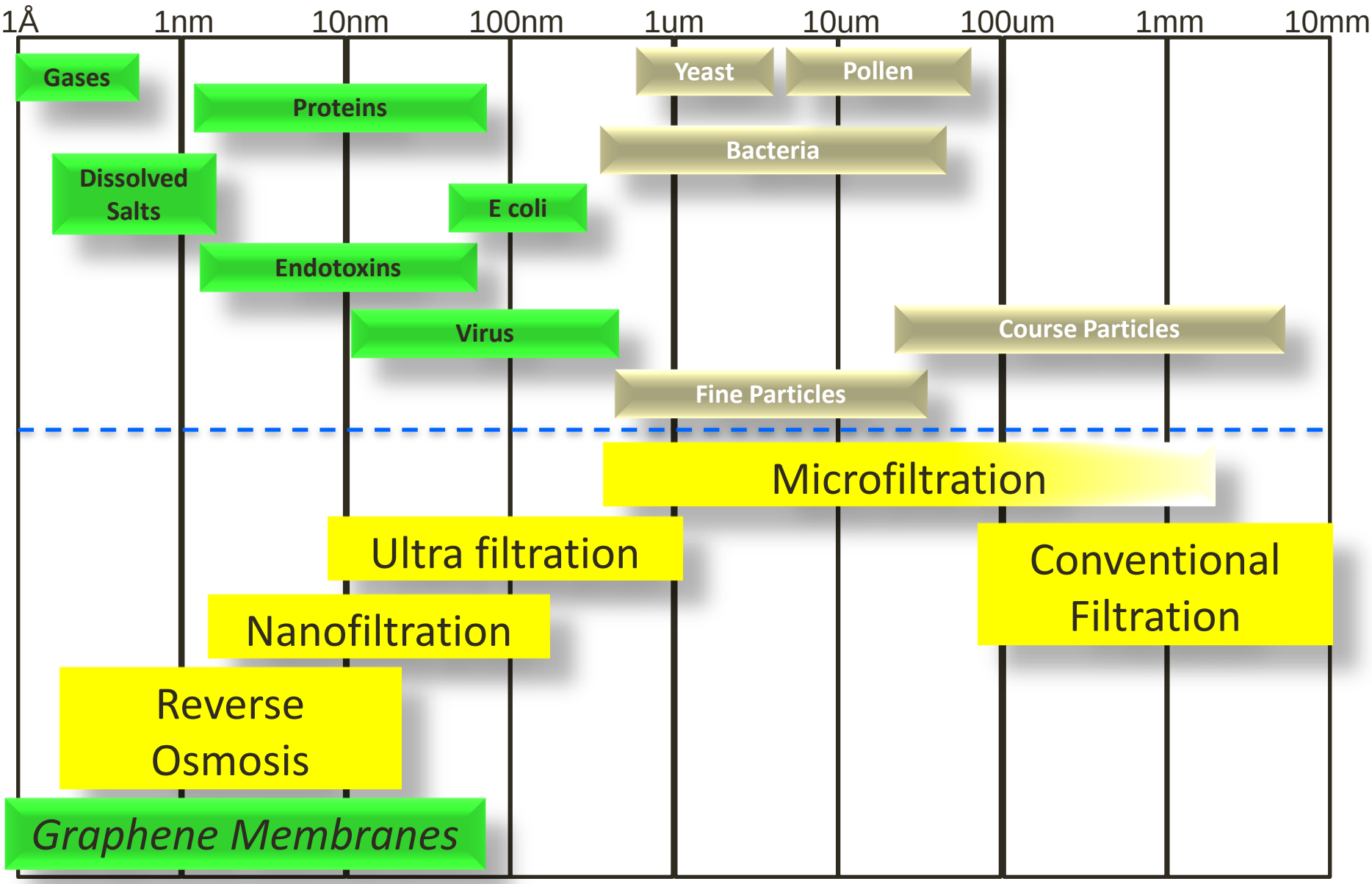
Nature Nanotechnology, **2015**

Grossman Group (MIT)

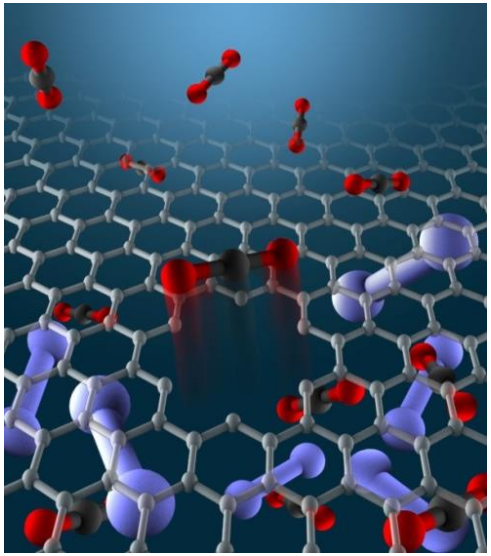
Cohen Tanugi., et al.

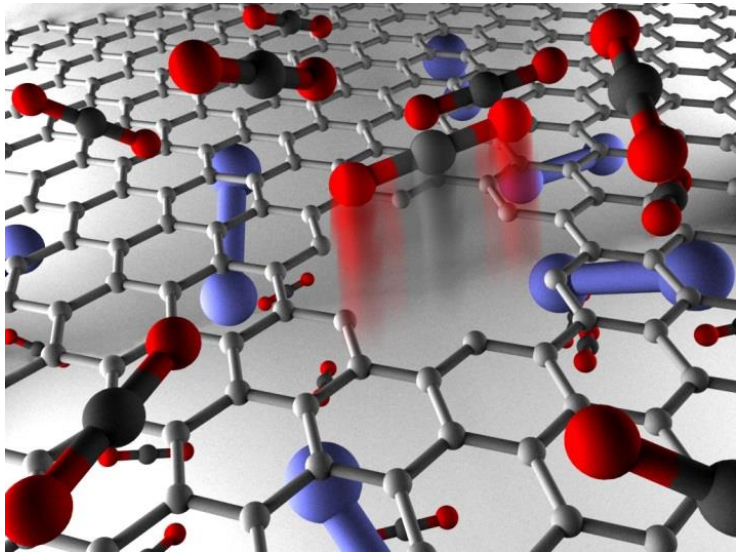
Nano Lett., **2012**,

Membrane Filtration



Outline





Molecular Transport through Porous Graphene

S.P. Koenig et al., *Nature Nanotechnology,* **7**, 728-732 (2012)

L. Wang et al., *in review* (2015)

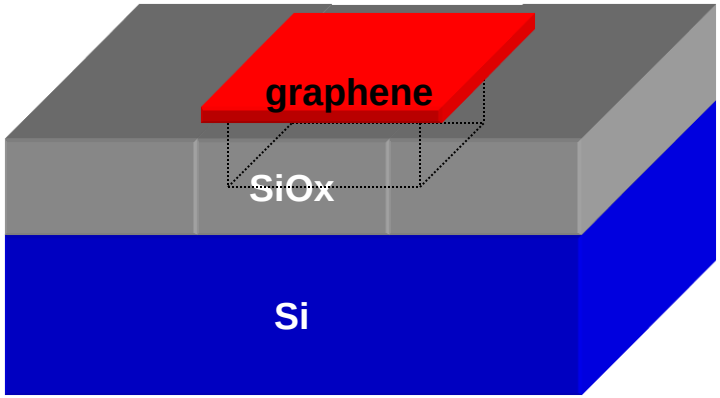
Liquid Ion Transport through Graphene

See Lauren Cantley's poster at 5pm

L. Cantley et al., *in preparation* (2015)

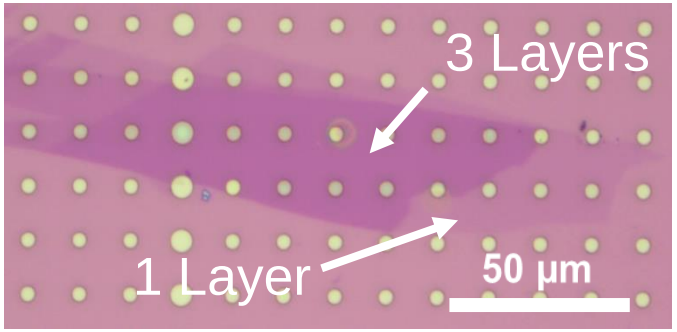
Suspended Graphene

depth ~ 300 nm diameter ~ 5 µm



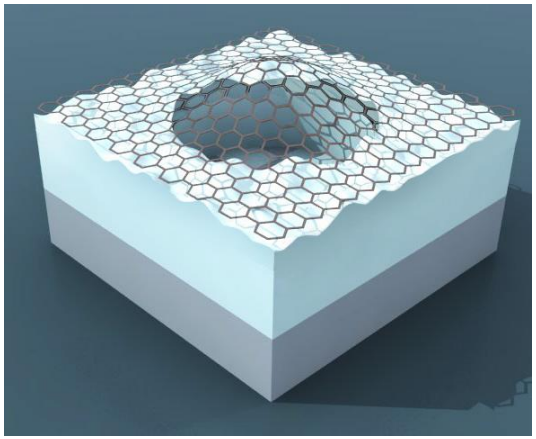
Clamping by van der Waals force

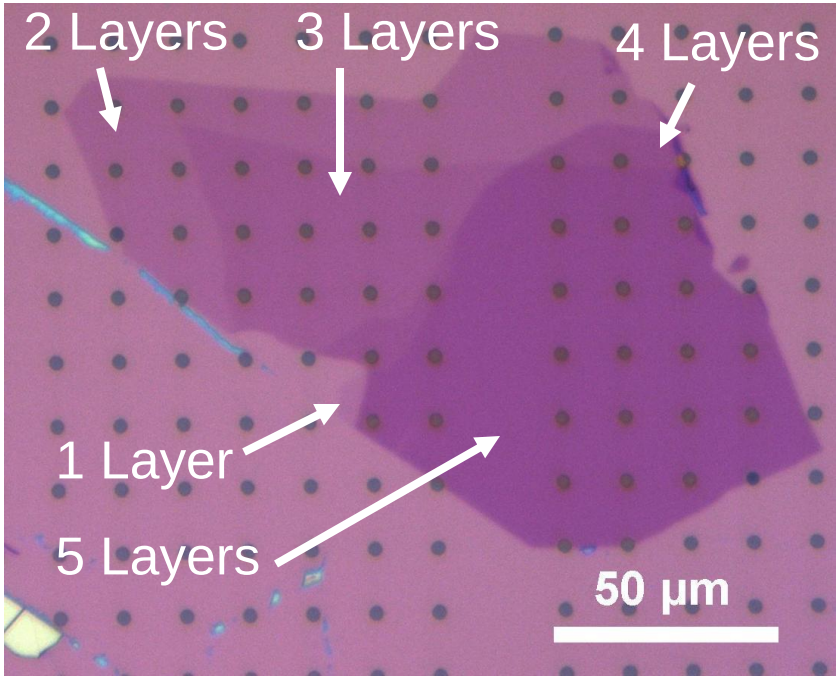
Layer number verified by Raman Spectroscopy



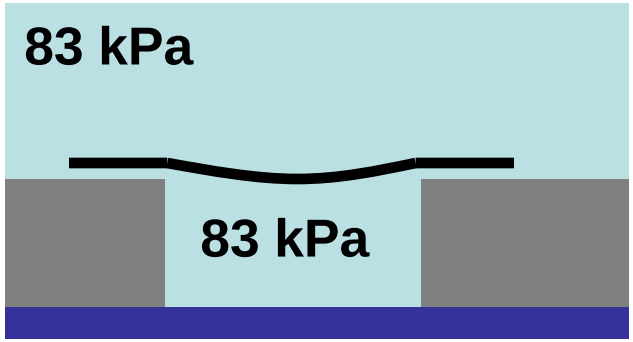
Geim and Novoselov – "Scotch Tape Method"

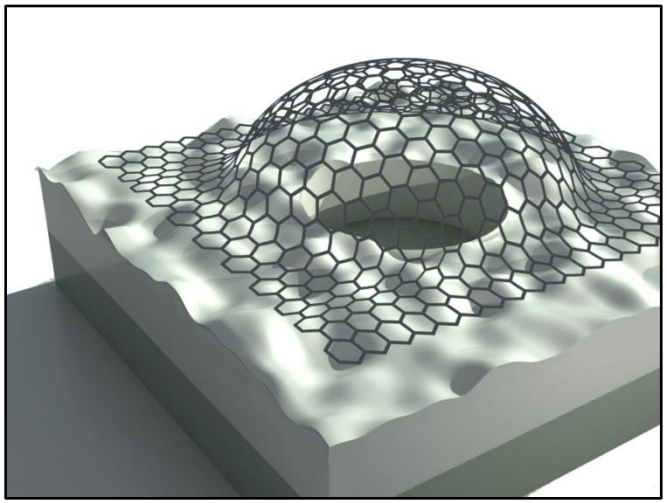
Graphene sealed microcavity



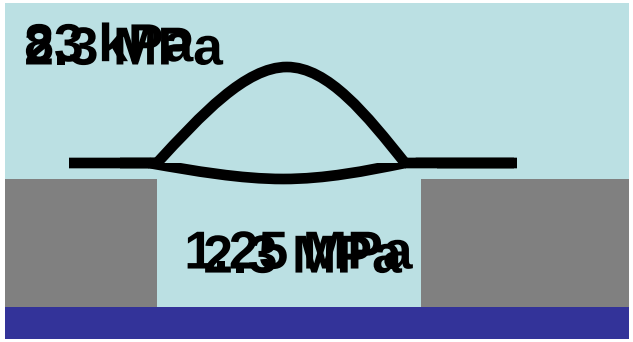


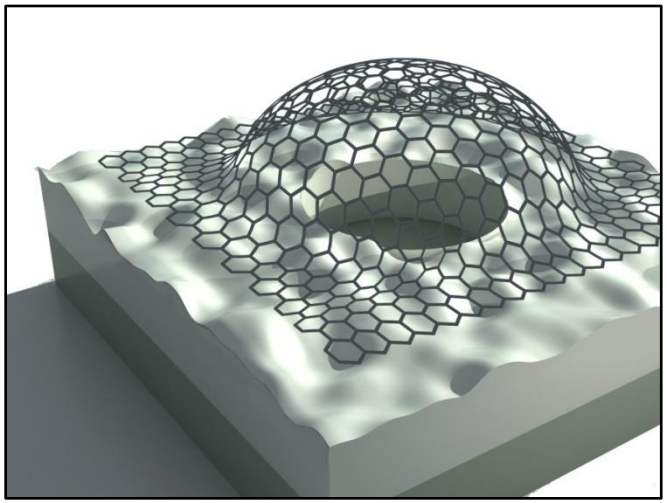
Atomic Membrane as a Barrier





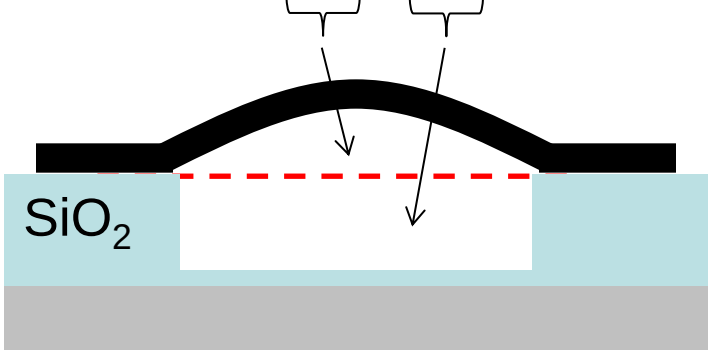
Atomic Membrane as a Barrier



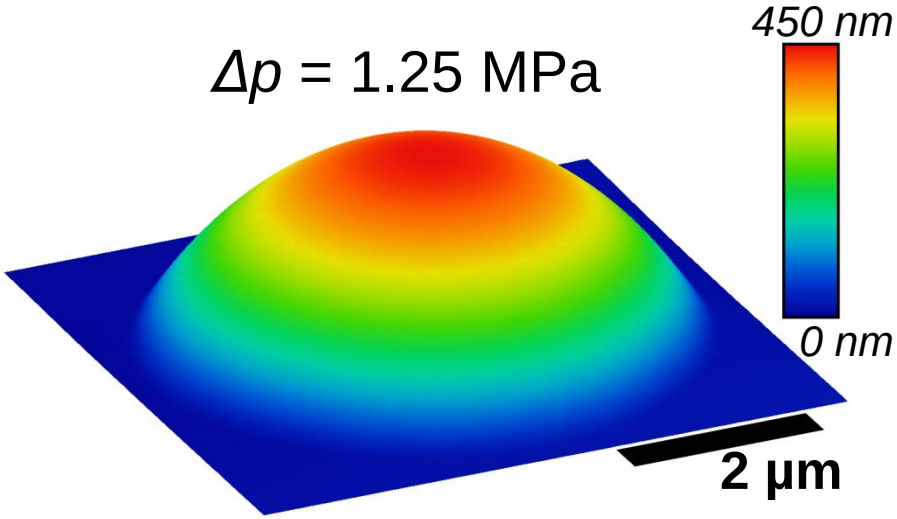


Isothermal Expansion

$$P_0V_0 = P_i(V_b + V_0) = nRT$$



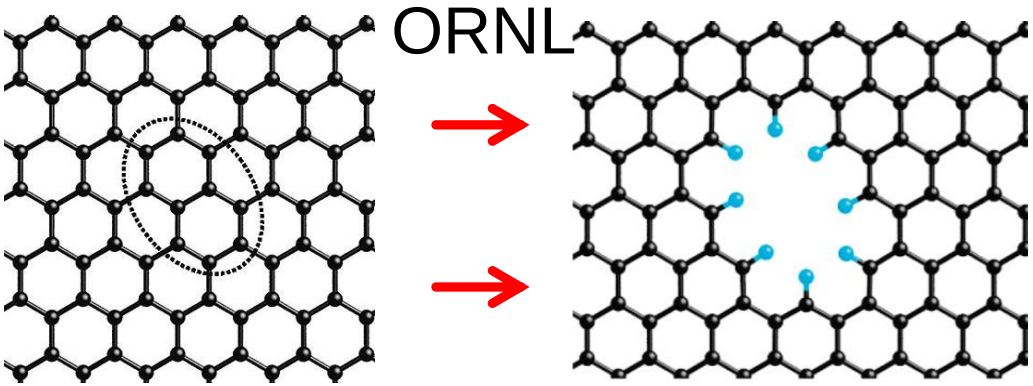
Bunch, J.S. et al. Impermeable atomic membranes from graphene sheets. *Nano Lett.* **8**, 2458-2462 (2008)

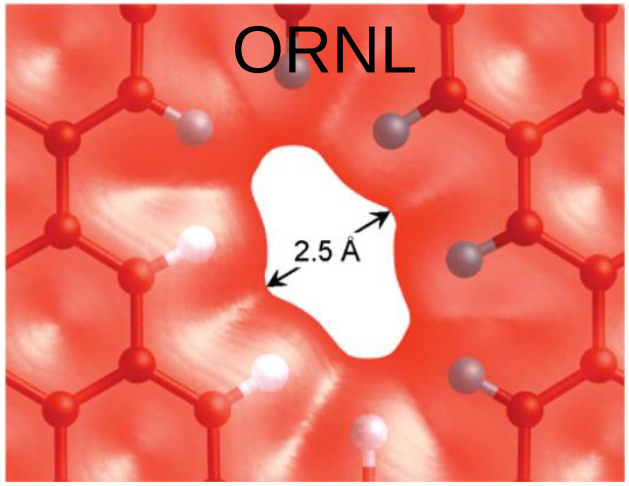


Atomic Force Microscope (AFM) Scan

1 Atom Thin Barrier – World's Thinnest Balloon!

Graphene Gas Separation Membranes

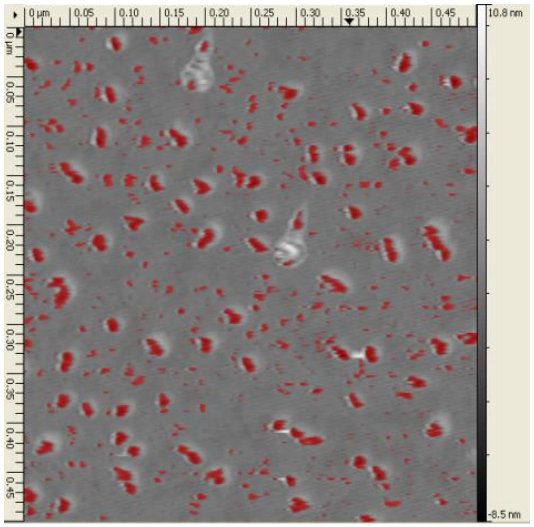


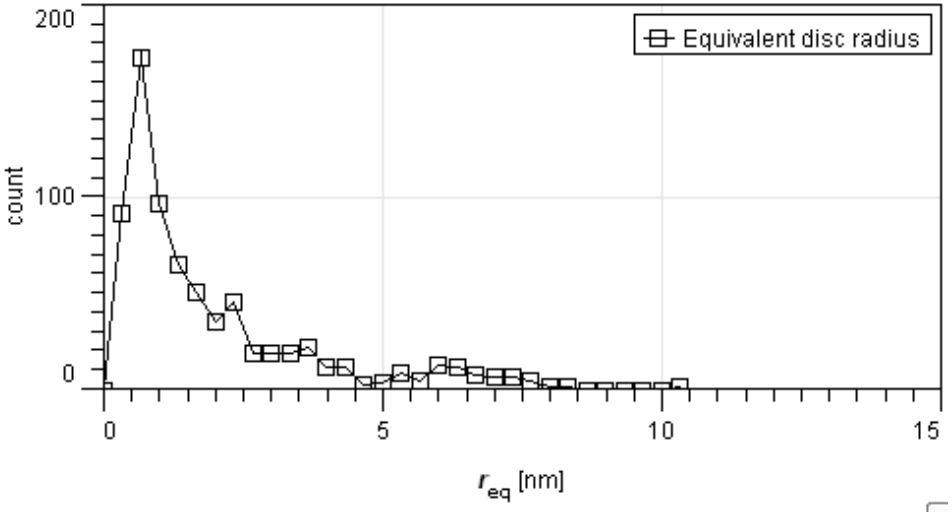


Modeling of Graphene Membranes from ORNL:

- ~10^{20} higher selectivity
- ~10^{7} higher permeability
  (over state of the art silica membranes)

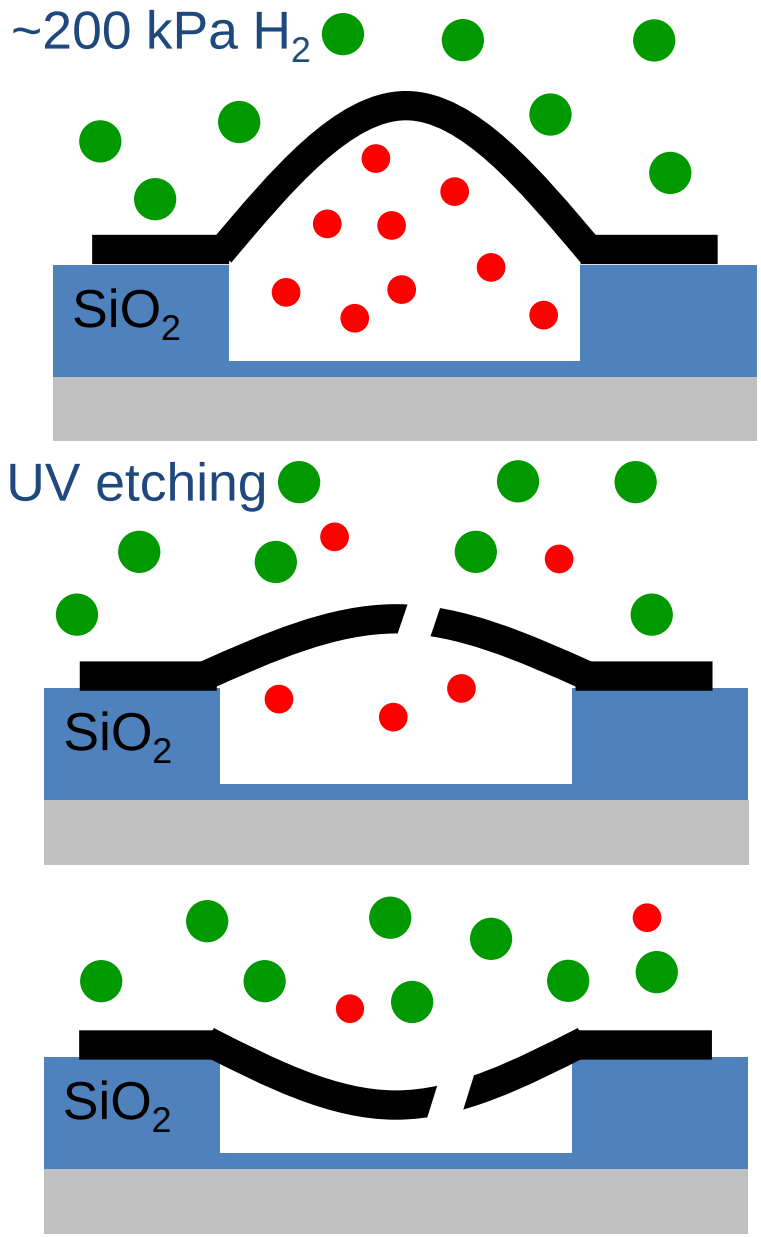
D. Jiang, V.R. Cooper, and S. Dai
Nano Lett. **9**, 4019-4024 (2009).

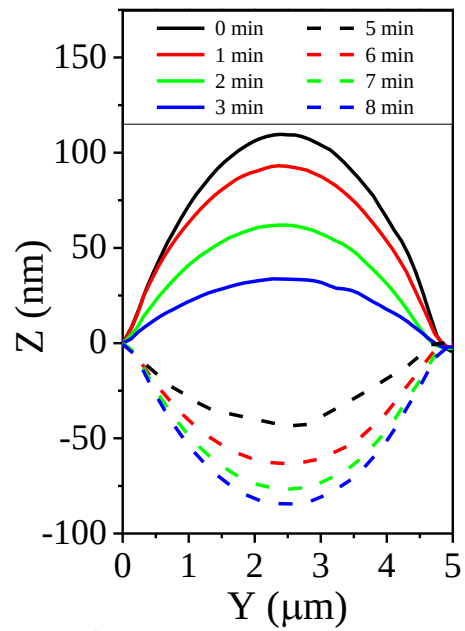


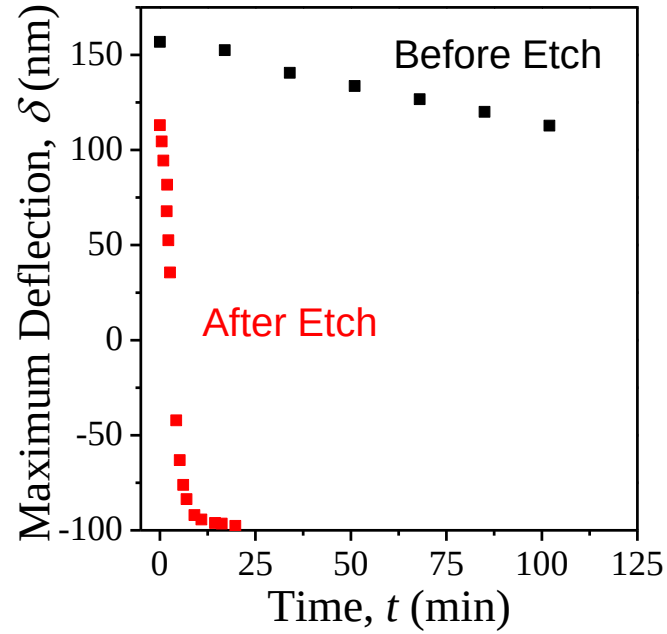


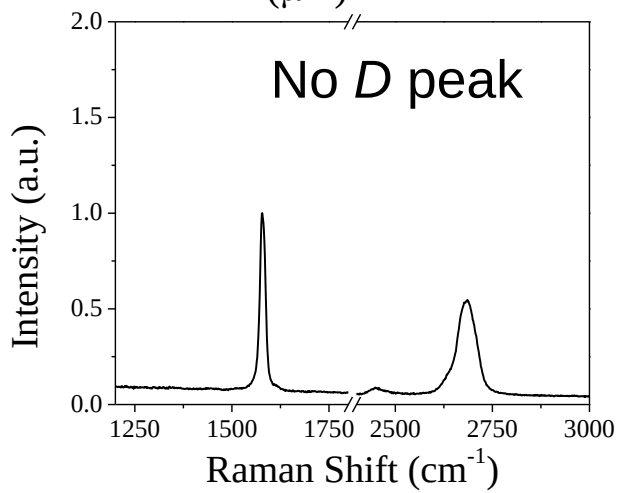
Etching small holes in graphene using UV etching

Making Angstrom Size Pores



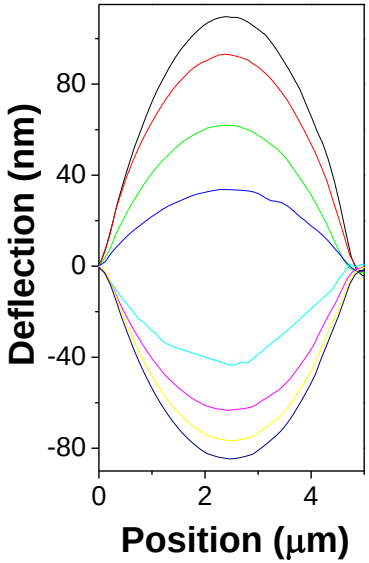


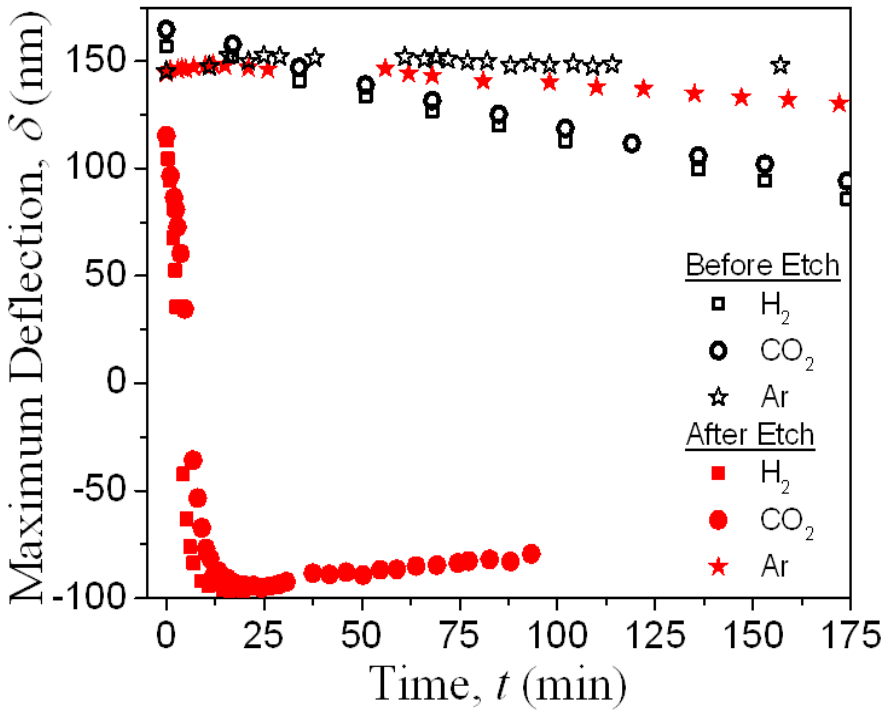


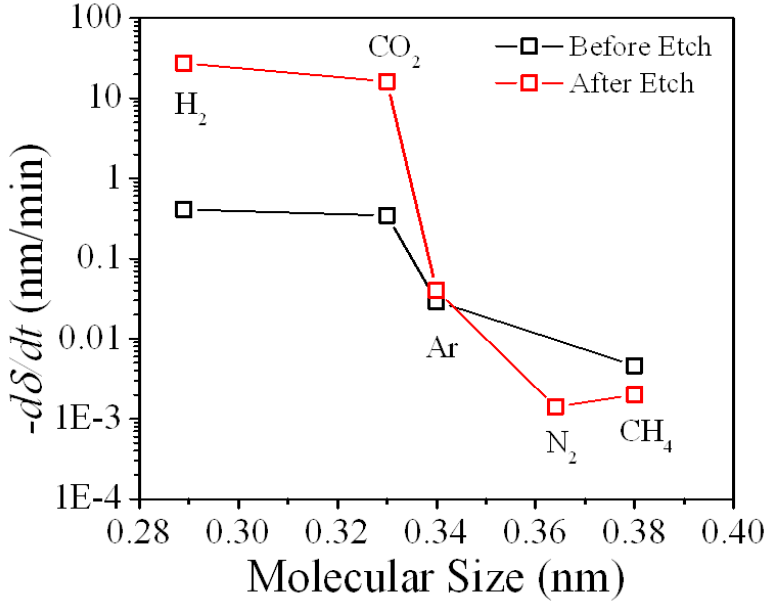


S.P. Koenig et al., Nature Nanotechnology, **7**, 728-732 (2012)

CO_2/Argon Gas Separation







Molecular cut off ~ 3.4 Å!

For sieving ~10 nm particles with CVD Graphene see: Karnik Group (MIT), S.C. O'Hern et al. ACS Nano (2012)

S.P. Koenig et al., Nature Nanotechnology, **7**, 728-732 (2012)

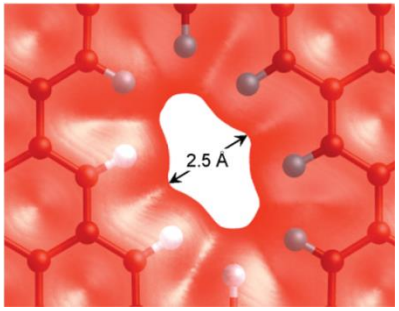
Gas Separation through Atomic Pores in Atomic Membrane!

Leak Rate through Porous Graphene

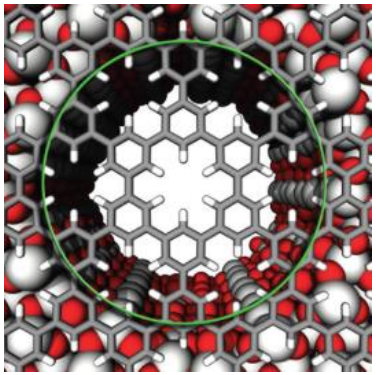
$$d\delta/dt \longrightarrow dn/dt$$

$$\frac{dn}{dt} = \frac{[3K(Ew\delta^2)/a^4 \cdot V(\delta) + P(C\pi a^2)]}{RT} \cdot \frac{d\delta}{dt}$$

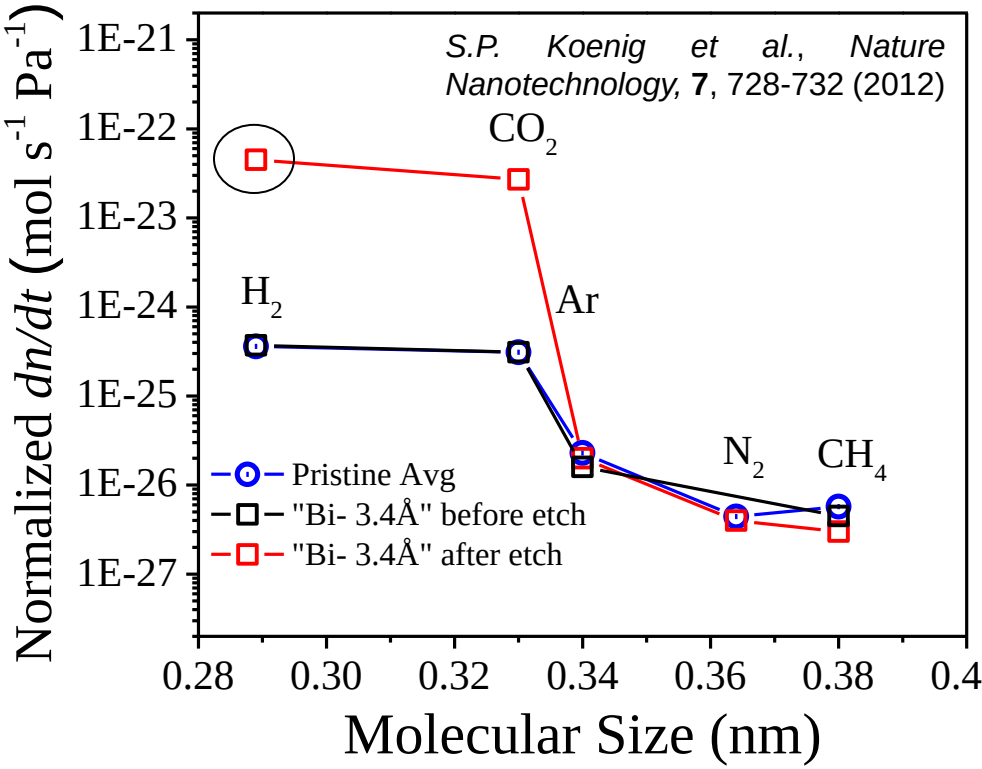
Theory: Hydrogen Terminated Pores



D. Jiang, V.R. Cooper, and S. Dai *Nano Lett.* **9**, 4019-4024 (2009).



S. Blankenburg, *et al.* Porous graphene as an atmospheric nanofilter. *Small* **6**,



2 missing Benzene Rings

H_2/CH_4 selectivity

1 missing Benzene Ring

H_2/CO_2 selectivity

H_2/Ar selectivity

H_2 Permeance

$10^{-20}\ mol\ s^{-1} Pa^{-1}$

$10^{-24}\ mol\ s^{-1} Pa^{-1}$

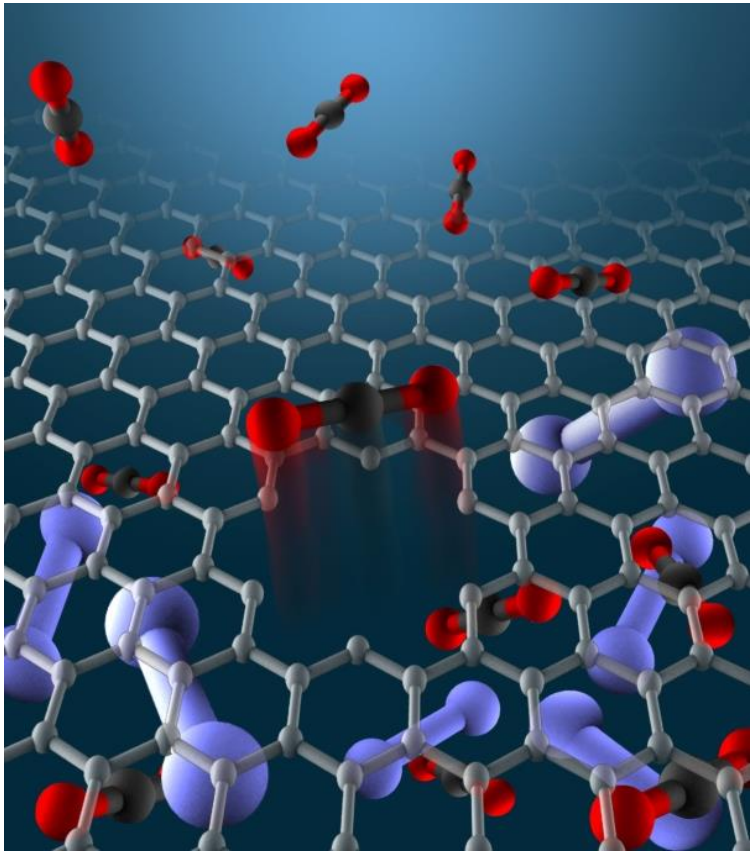
$4.5 * 10^{-23}\ mol\ s^{-1} Pa^{-1}$

Pore size and chemistry important!

Summary – Graphene Separation Membranes

- Selective Molecular Sieving through Porous Graphene Membranes
- Nanopore Molecular Valves in Graphene
- Ion Transport through Porous Graphene

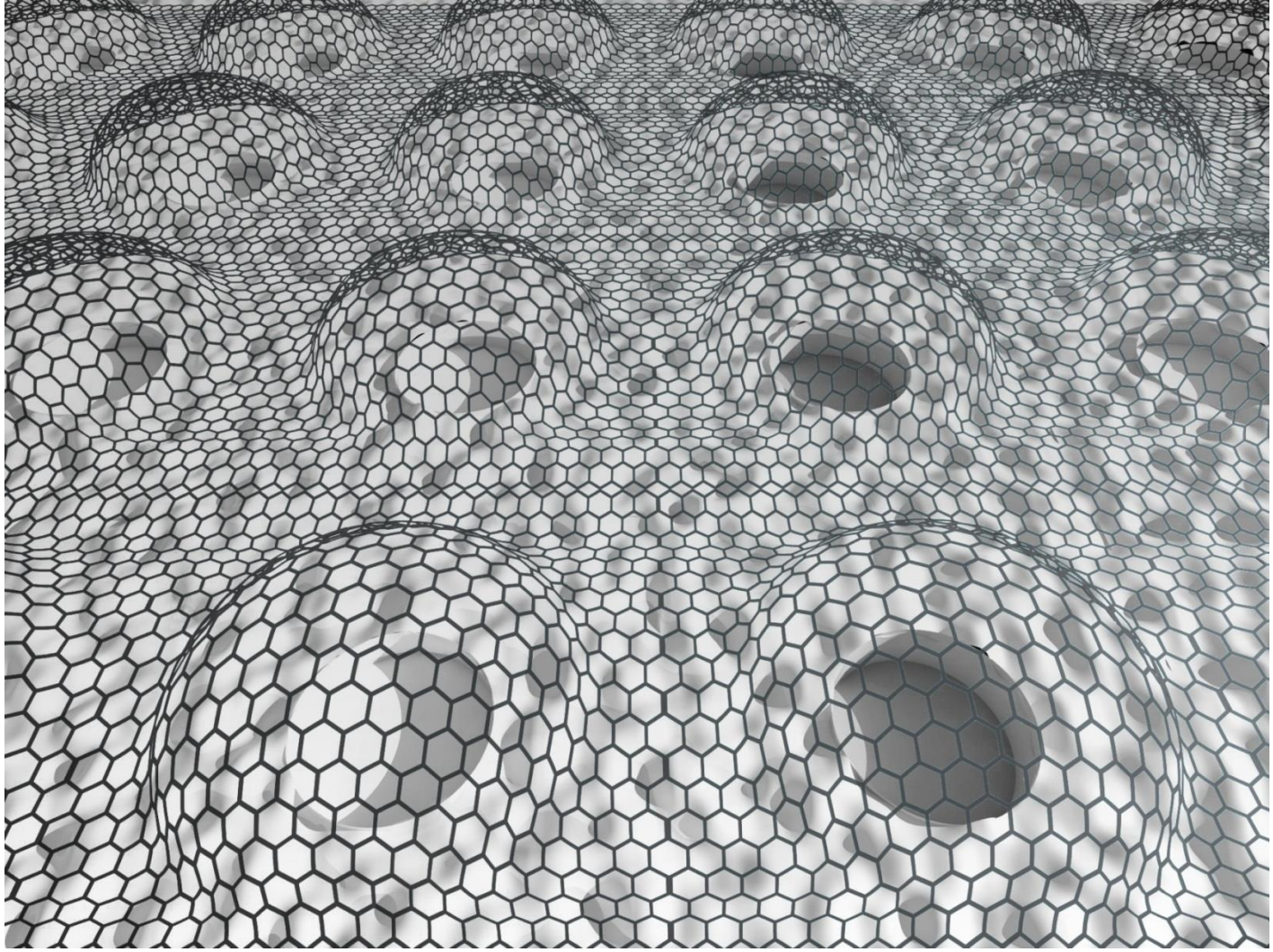




S.P. Koenig et al., *Nature Nanotechnology,* **7**, 728-732 (2012)

L. Wang et al., *in review* (2015)

L. Cantley et al., *in preparation* (2014)



Thank you!

Questions?