Atomic and Molecular Separation through Porous Graphene

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Support:
NSF, DARPA, CU, BU
Carbon vs. Silicon

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

Mechanical
$12 Billion business
12% annual growth

Electrical
~ $1 Trillion business
**Carbon vs. Silicon**

**Superior Properties**
- Electrical
- Mechanical
- Thermal

**Different Bonding**
- Graphite
- Graphene/Nanotubes

**Diamond**
- Apollo Diamonds
Nanotubes

1997

Electronic

Mechanical

1997

Chemical/Biological

Graphene

2006

Electrical

2009

Mechanical

Chemical/Biological

2010
Graphene (Electrical)

Manchester (Novoselov, Geim, et al.)

Gate Dependent Transport

Integer Quantum Hall Effect

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

**Molecular Separation**

Thin membrane

Well defined pores

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Graphene as a Membrane

Gas Separation: control what molecules pass


**ORNL**

**Karnik Group (MIT) - CVD**
ACS Nano, 6, 10130-10138 (2012).

**Hobum Park Group (Korea)**

**Miao Yu (Univ South Carolina)**

**Hyung Gyu Park (ETH Zurich)**

DNA Sequencing

**Golovchenko Group (Harvard Univ.)**
*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

**Geim Group (Univ. of Manchester) - GO**

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

**Karnik Group (MIT) - CVD**

**O’Hern S., et al.**

**ORNL**
Surwarde., et al.
*Nature Nanotechnology*, 2015

**Grossman Group (MIT)**
Cohen Tanugi., et al.
*Nano Lett.*, 2012,
Molecular Transport through Porous Graphene


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

Graphene sealed microcavity

Clamping by van der Waals force
Layer number verified by Raman Spectroscopy

Geim and Novoselov – “Scotch Tape Method”
Atomic Membrane as a Barrier

83 kPa

83 kPa

Diagram showing the atomic membrane as a barrier with a pressure difference of 83 kPa across it.
Atomic Membrane as a Barrier

Isothermal Expansion

\[ P_0 V_0 = P_i (V_b + V_0) = nRT \]

\[ \Delta \rho = 1.25 \text{ MPa} \]


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

~200 kPa H₂

UV etching

SiO₂

Before Etch

After Etch

No D peak

CO₂/Argon Gas Separation

Molecular cut off ~ 3.4 Å!


Gas Separation through Atomic Pores in Atomic Membrane!
Leak Rate through Porous Graphene

\[
d\delta/dt \rightarrow dn/dt
\]

\[
\frac{dn}{dt} = \left[ \frac{3K(E_w\delta^2)}{a^4 \cdot V(\delta) + P(C\pi a^2)} \right] \cdot \frac{d\delta}{dt}
\]

Theory: Hydrogen Terminated Pores

2 missing Benzene Rings

H₂/CH₄ selectivity

1 missing Benzene Ring

H₂/CO₂ selectivity

H₂ Permeance

\(10^{-20} \text{ mol s}^{-1} \text{ Pa}^{-1}\)

\(10^{-24} \text{ mol s}^{-1} \text{ Pa}^{-1}\)

4.5 \(\times\) \(10^{-23}\) \text{ mol s}^{-1} \text{ Pa}^{-1}

Pore size and chemistry important!


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

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

H₂, Ar, CO₂, N₂, CH₄

H₂/Ar selectivity

H₂/CO₂ selectivity

H₂ Permeance
Summary – Graphene Separation Membranes

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

L. Wang et al., in review (2015)
L. Cantley et al., in preparation (2014)
Thank you!
Questions?