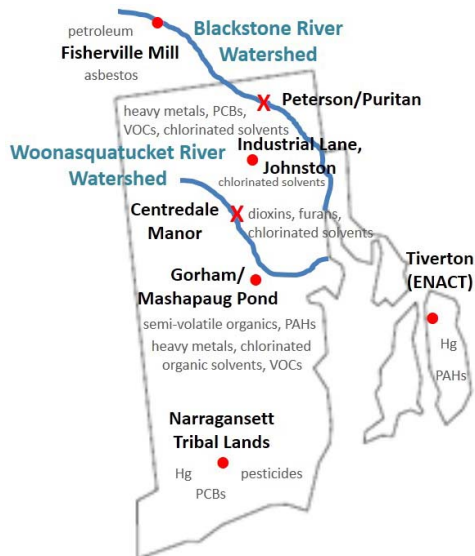


Brown University Superfund Research Program

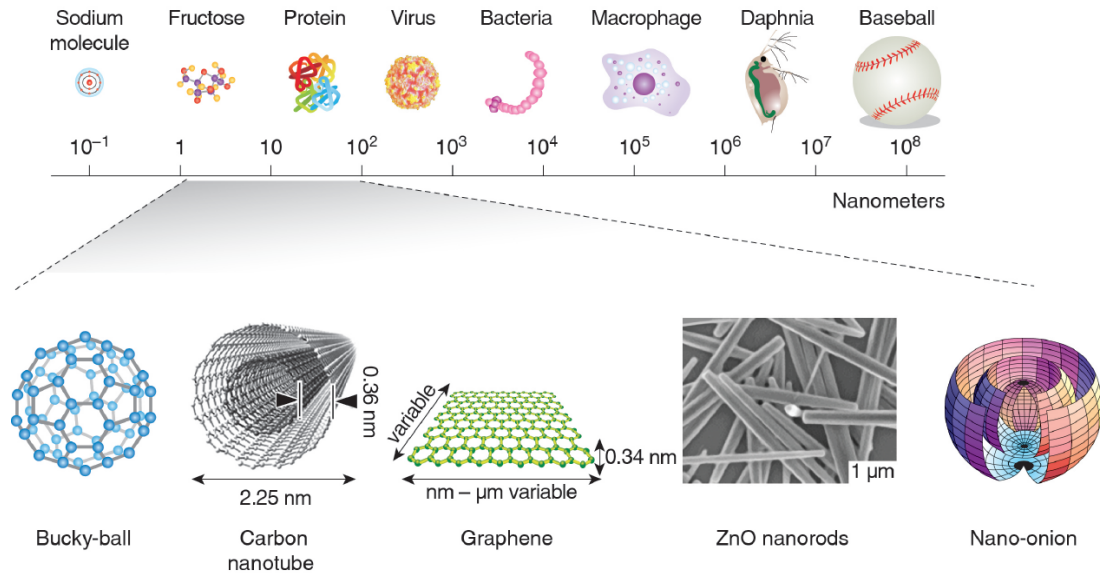
Nano-Enabled Technologies for Environmental Health

Robert Hurt, Brown University



Nanotechnology

Working at the atomic, molecular and supramolecular levels, in the length scale of approximately 1-100 nm range, in order to understand and create materials, devices and systems with fundamentally new properties and functions because of their small structure.
Definition from <http://nano.gov>

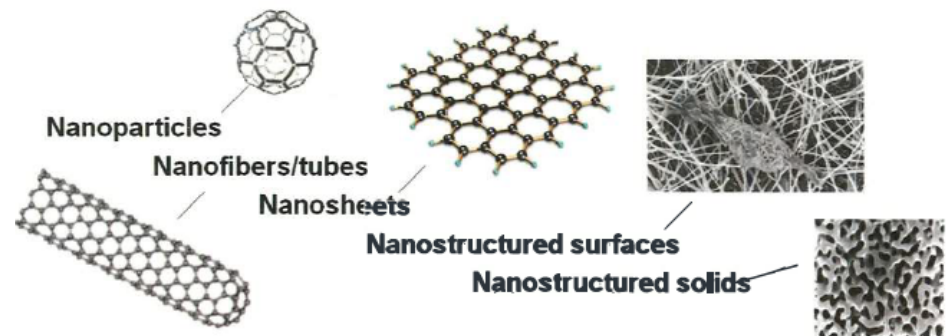


A toolkit of new materials for environmental applications

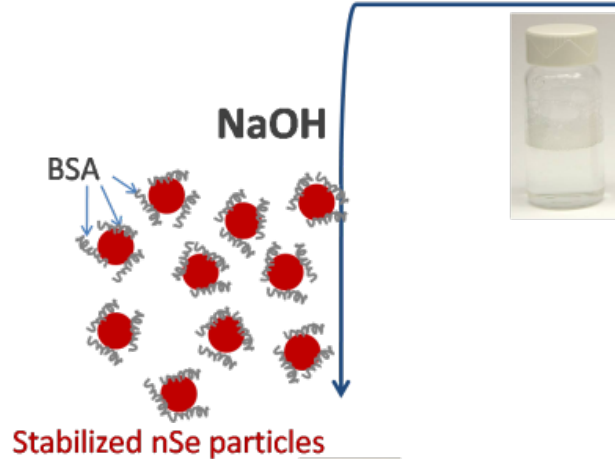
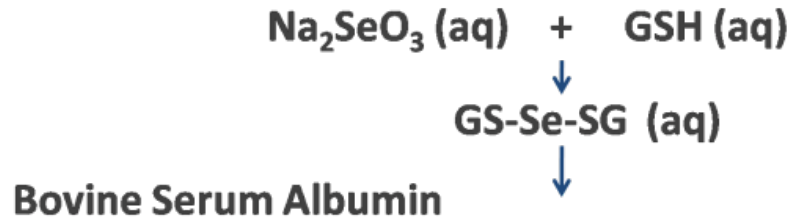
Periodic Table of Elements

1 H																	2 He						
3 Li	4 Be																	5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg																	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr						
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe						
55 Cs	56 Ba	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu							
87 Fr	88 Ra	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr							

*Lanthanide Series
+ Actinide Series

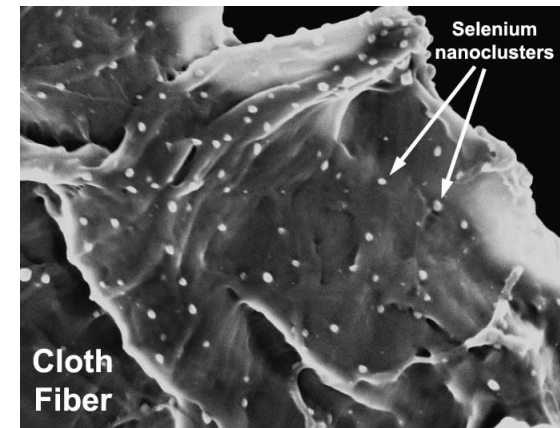


Case Study: Nano-selenium for Hg capture



Dry or freeze-dry
to powder

selenium
nanoclusters
on cellulose
fiber surfaces



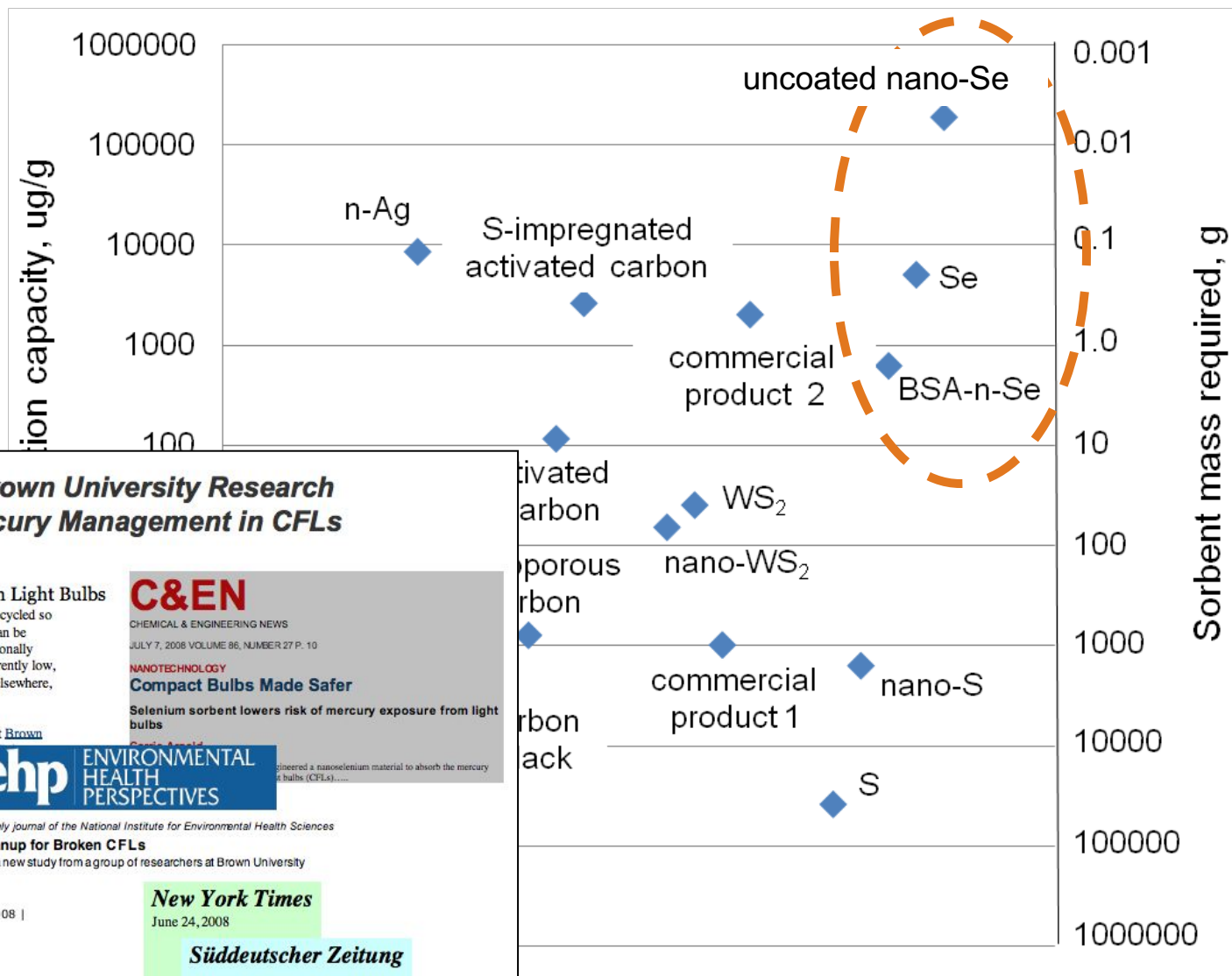
capillary uptake
into porous medium

drying



Case Study: Nano-enabled Hg capture

Uncoated nano-Se is 70 x more active than the best commercial sorbent !



The New York Times

July 8, 2008

Observatory

A Cloth to Cut the Mercury Risk From Light Bulbs



Compact fluorescents are supposed to be recycled so that the mercury (which is in vapor form) can be dealt with properly. But the tubes do occasionally crack or break, and the recycling rate is currently low, so mercury could be released in homes or elsewhere, posing a small risk to children.

Robert H. Hurt, an engineering professor at Brown University, along with a student, Natali...

Brown University Research on Mercury Management in CFLs

C&EN

CHEMICAL & ENGINEERING NEWS
JULY 7, 2008 VOLUME 86, NUMBER 27 P. 10

NANOTECHNOLOGY

Compact Bulbs Made Safer

Selenium sorbent lowers risk of mercury exposure from light bulbs

David Asmund

ehp

**ENVIRONMENTAL
HEALTH
PERSPECTIVES**

monthly journal of the National Institute for Environmental Health Sciences

Cleanup for Broken CFLs

..... a new study from a group of researchers at Brown University

**nature
nanotechnology**

Research Highlights

Nature Nanotechnology Published online: 11 July 2008 |
doi:10.1038/nnano.2008.230

Nanomaterials: Mercury mop

Al Lin Chun

Abstract

Nanoscale formulations of selenium and silver can capture mercury vapours from broken compact fluorescent lamps more efficiently than their microscale counterparts....

New York Times

June 24, 2008

Süddeutsche Zeitung

Providence Journal

July 1, 2008, Solution offered for mercury disposal

July 2, 2008, Brown bulb breakthrough

Financial support

NCIAA – National Collegiate
Inventors and Innovators Alliance

NSF STTR – Small Business
Technology Transfer

STAC – Rhode Island
Science and Technology Council

Banyan Environmental

– a SRP spin-off technology start-up



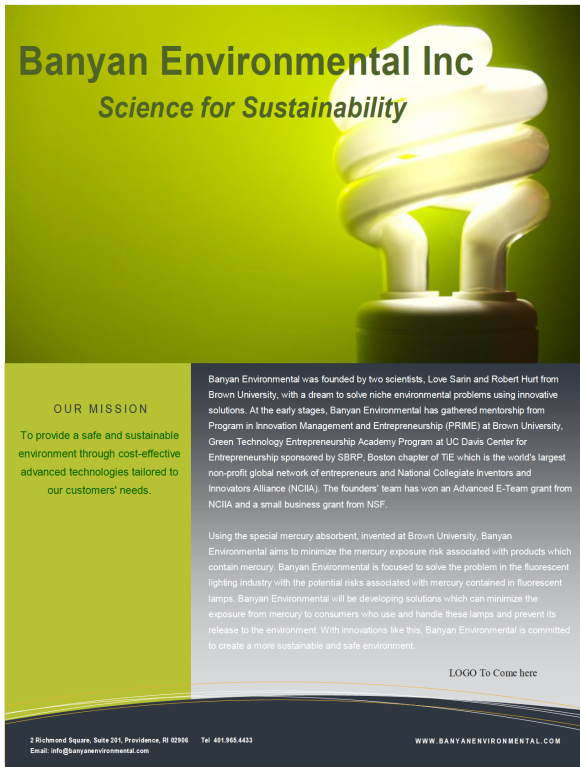
Dr. Love Sarin
CEO
(former SRP trainee)



Ruben Spitz-Steinberg
R&D engineer



John Moorhead
Finance, Business Development



Banyan Environmental Inc
Science for Sustainability

OUR MISSION

To provide a safe and sustainable environment through cost-effective advanced technologies tailored to our customers' needs.

Banyan Environmental was founded by two scientists, Love Sarin and Robert Hurt from Brown University, with a dream to solve niche environmental problems using innovative solutions. At the early stages, Banyan Environmental has gathered mentorship from Program in Innovation Management and Entrepreneurship (PRIME) at Brown University, Green Technology Entrepreneurship Academy Program at UC Davis Center for Entrepreneurship sponsored by SBRP, Boston chapter of TIE which is the world's largest non-profit global network of entrepreneurs and National Collegiate Inventors and Innovators Alliance (NCIA). The founders' team has won an Advanced E-Team grant from NCIA and a small business grant from NSF.

Using the special mercury absorbent, invented at Brown University, Banyan Environmental aims to minimize the mercury exposure risk associated with products which contain mercury. Banyan Environmental is focused to solve the problem in the fluorescent lighting industry with the potential risks associated with mercury contained in fluorescent lamps. Banyan Environmental will be developing solutions which can minimize the exposure from mercury to consumers who use and handle these lamps and prevent its release to the environment. With innovations like this, Banyan Environmental is committed to create a more sustainable and safe environment.

LOGO To Come here

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Email: info@banyanenvironmental.com WWW.BANYANENVIRONMENTAL.COM





Smart boxes, bags for safe recycling



Technologies for permanent
Hg sequestration

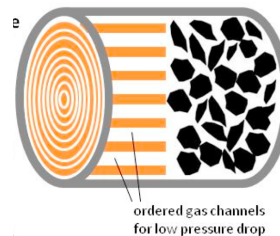
Nanoselenium as a Platform Technology



Retail drop-off boxes



Power plant flue gas capture

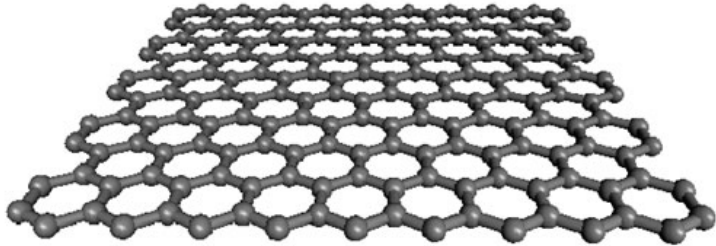


Cartridge-based air-cleaning
for NASA spaceflights



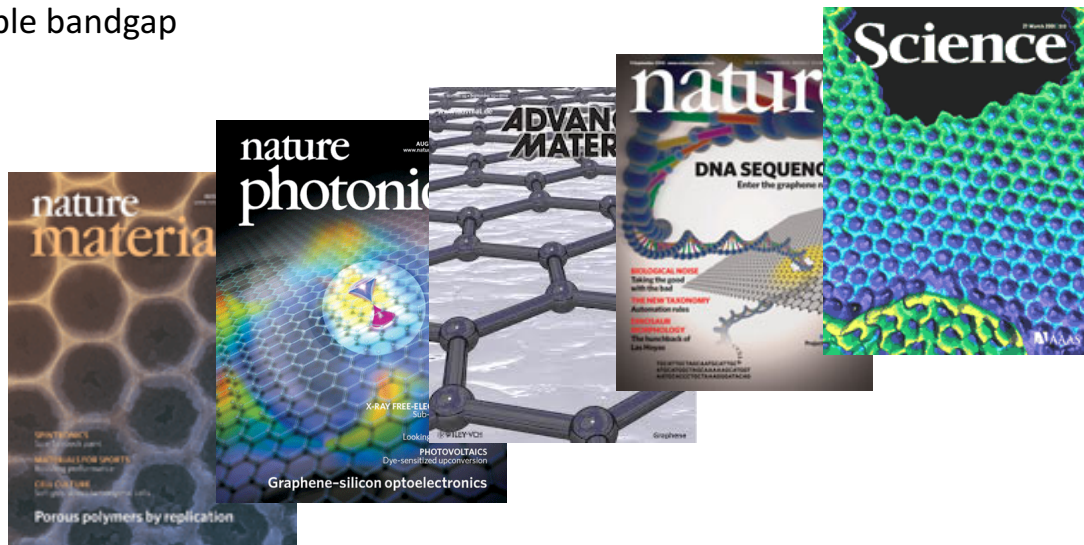
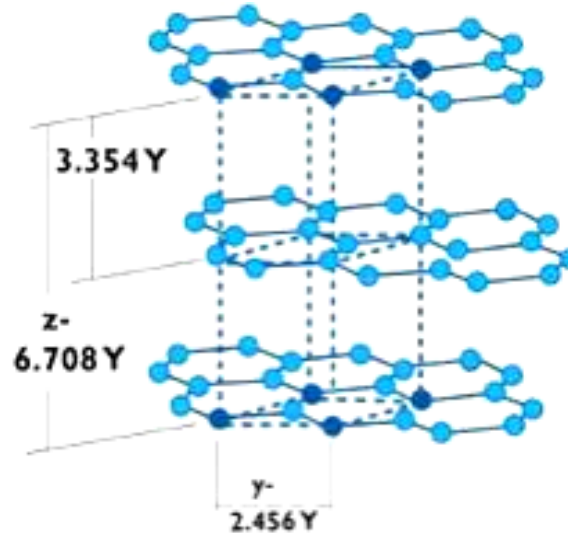
Consumer spill
and disposal kits

Case Study: Graphene-based Environmental Barriers



- first observed in 1962 (HP Boehm)
- first isolated in 2004 (Geim, Novoselov)
- led to the Nobel Prize, 2010 (Geim, Novoselov)

Exhibits: atomic thinness; high electron mobility;
high conductivity, optical transparency
tunable bandgap

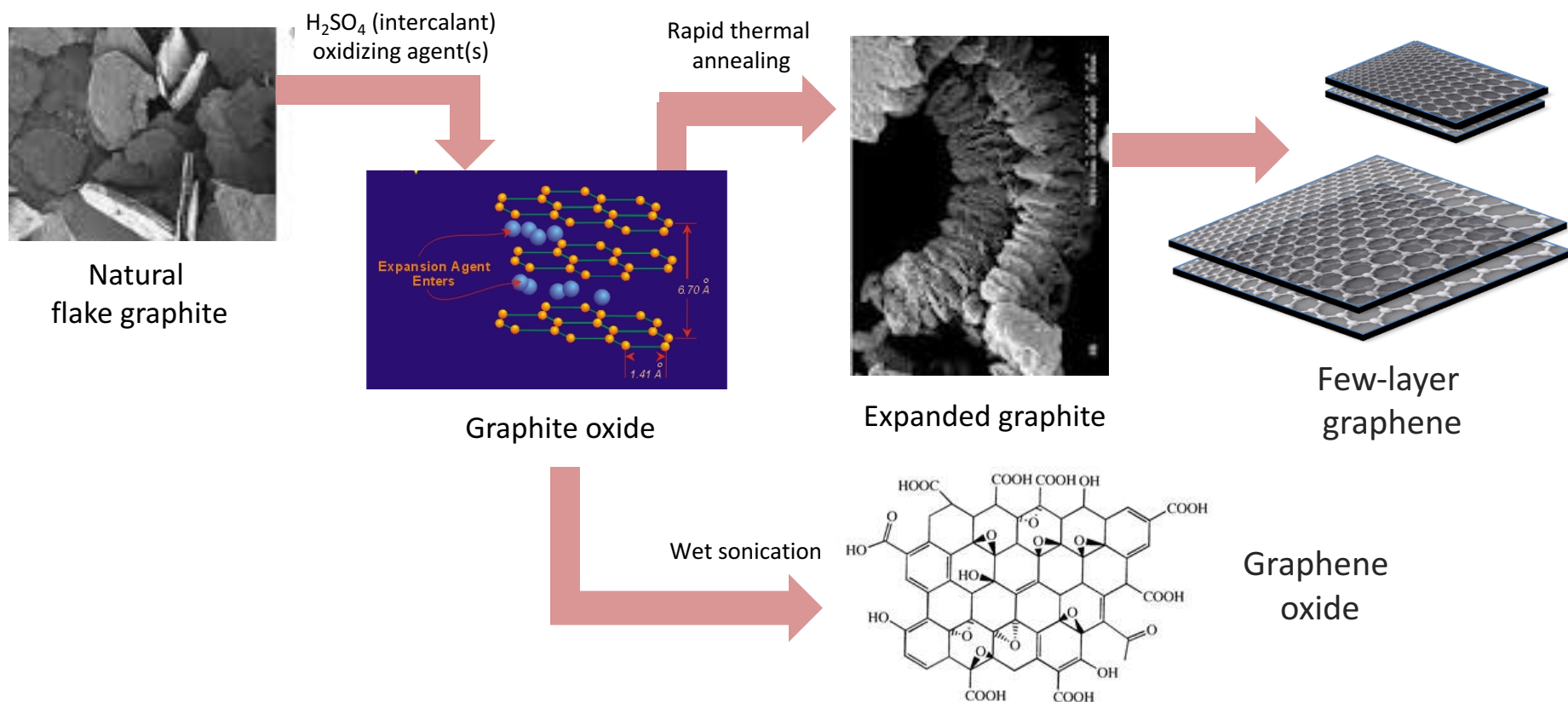


Pristine monolayer graphene
is typically fabricated by:

- mechanical exfoliation, or
- chemical vapor deposition

and used on substrates for
electronic applications

High-Volume-Production Graphene-Based Materials



Environmental Barrier Technologies

Many environmental technologies are based on *containment*

Engineered barriers are used to prevent toxicant release or transport to zones where human exposure is likely

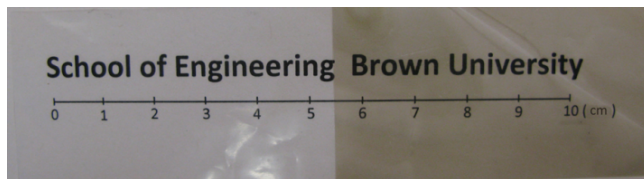
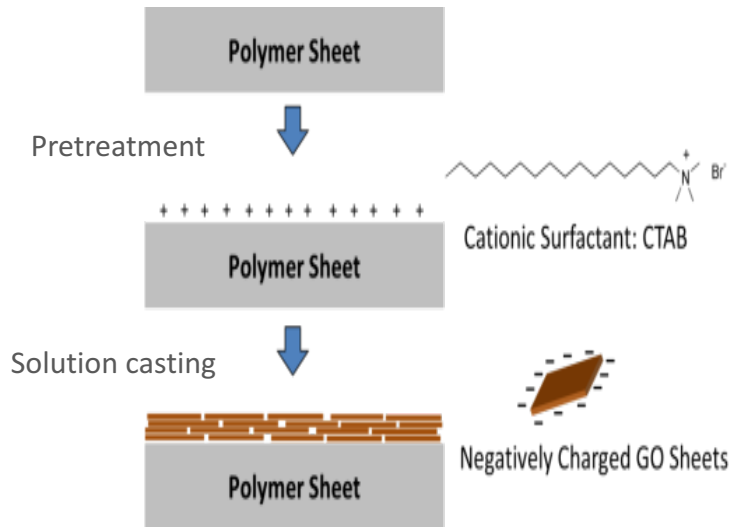
Environmental barriers include:

- geomembranes for landfill liners and caps [Rowe 2004]
- shipping and recycling of wastes containing volatile mercury [Johnson, 2008; Lee, 2009]
- barriers to “leachables and extractables” in food, beverage, and pharmacy products
- vertical subsurface barriers, horizontal vapor intrusion barriers
- functional layers in personal protective equipment for hazmat workers or military personnel



Graphene-Based Vapor Barriers

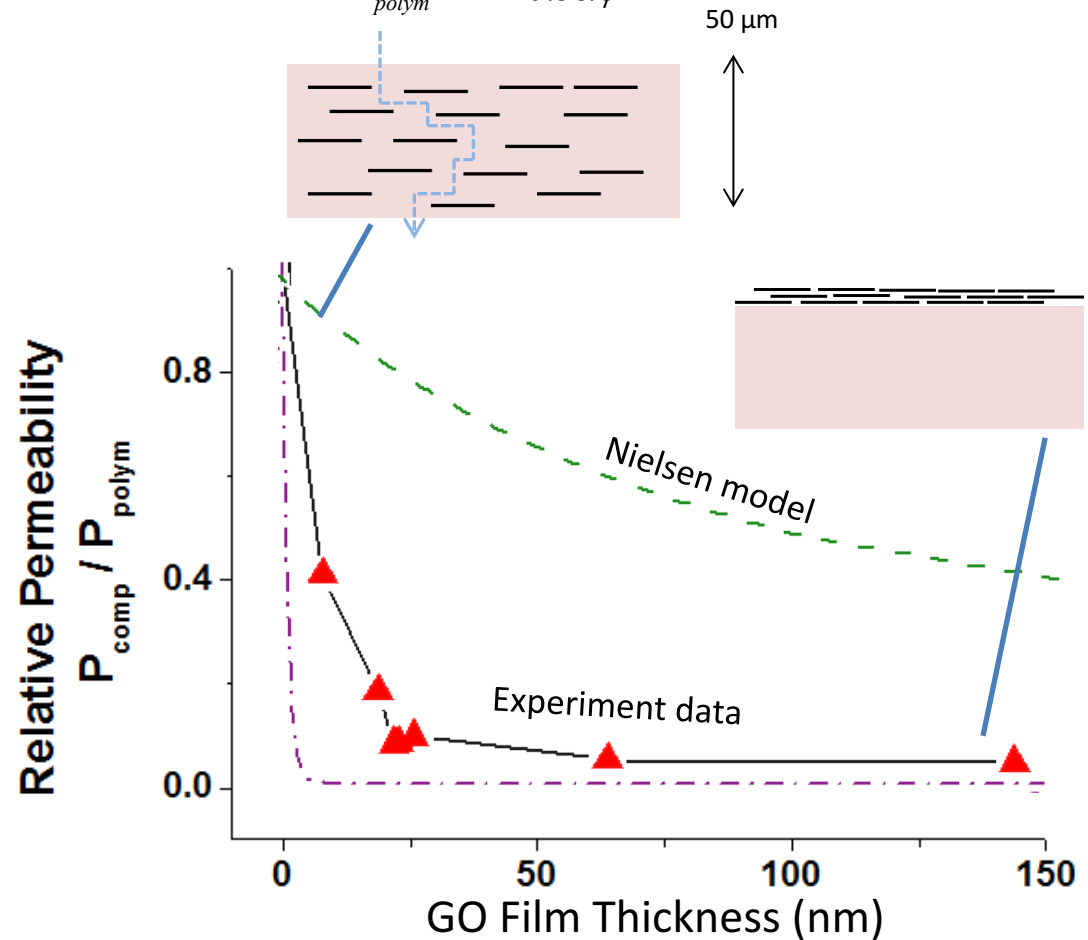
[Guo, Hurt et al., ES&T, 2012]



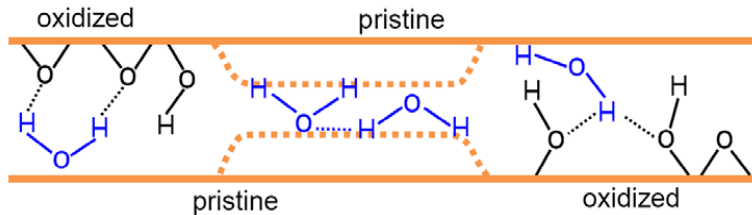
Without GO coating With GO coating

Data for Hg vapor

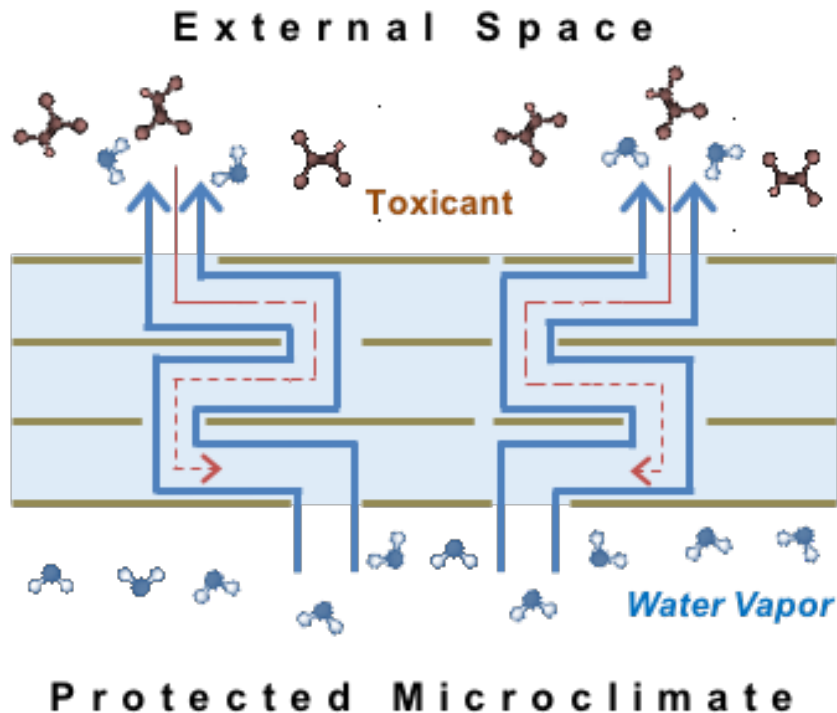
$$\frac{P_{comp}}{P_{polym}} = \frac{1 - \phi}{1 + 0.5\alpha\phi}$$



Water permeates “unimpeded” through graphene oxide films



(Nair *et al.*, Science, 2012)



Breathable toxicant barriers based on multilayer graphene oxide films



- In dry state, graphene oxide films reject all molecules (incl. He)
- In wet state, graphene oxide films reject molecules / substances with hydrated diameter > 9 Å

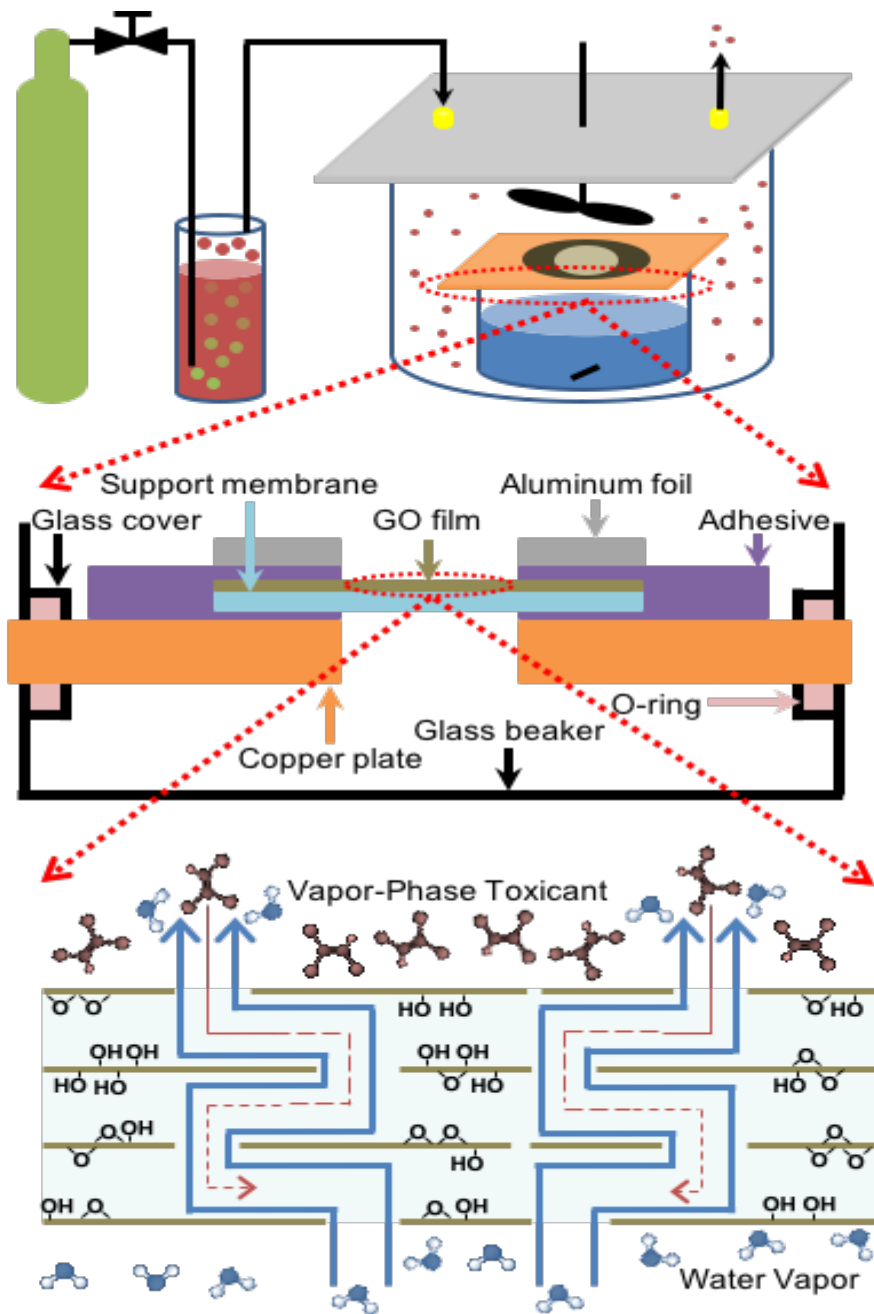
Open questions

- Barrier performance against small molecule toxicants
- Barrier performance during active water flow
- Practical suitability in breathable fabrics



Ruben Spitz
SRP Trainee
PhD Program, Brown

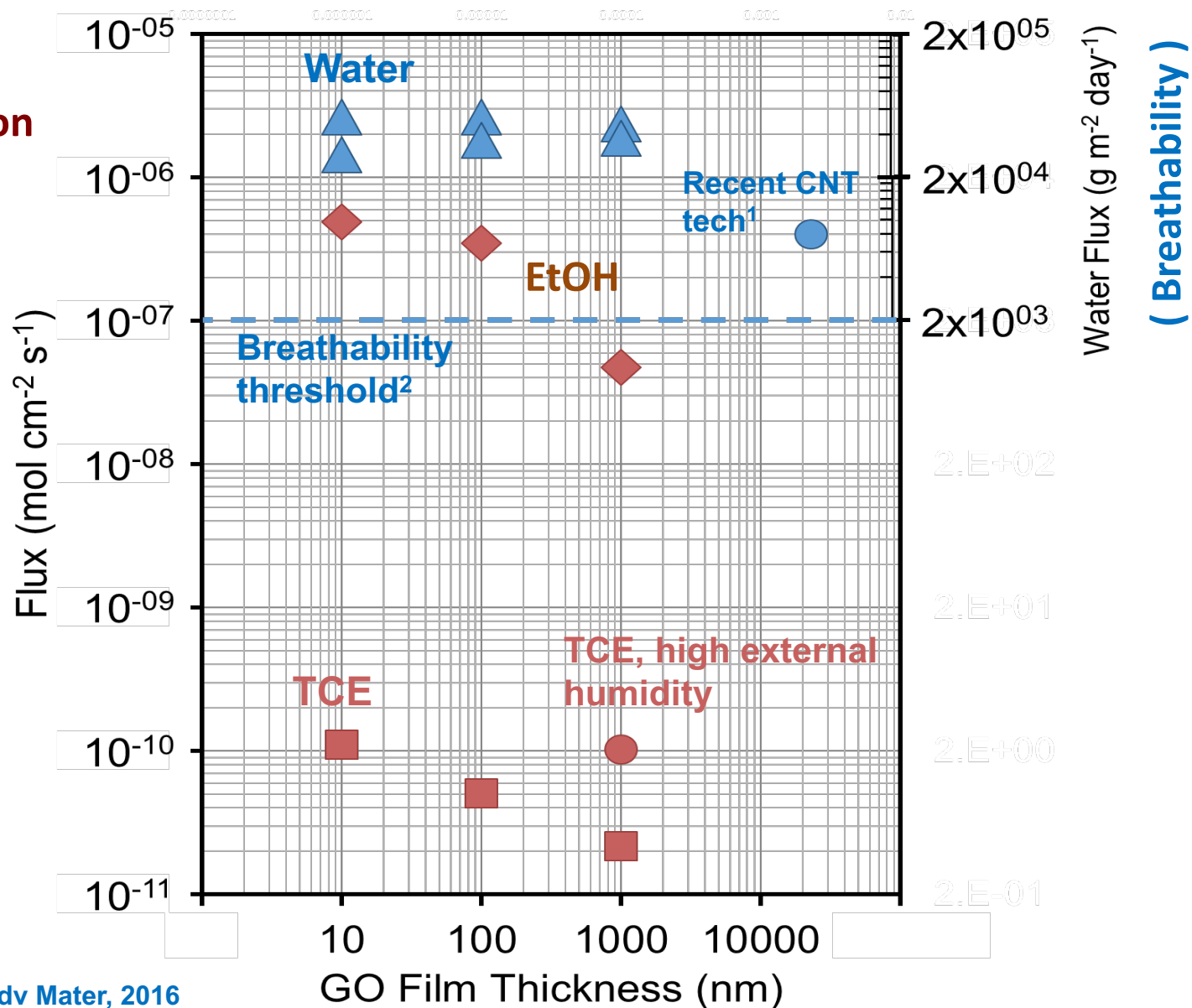
- Developed custom device for membrane testing with active water flux
- Selected TCE and ethanol as models of small molecule toxicants



Perspiration flux



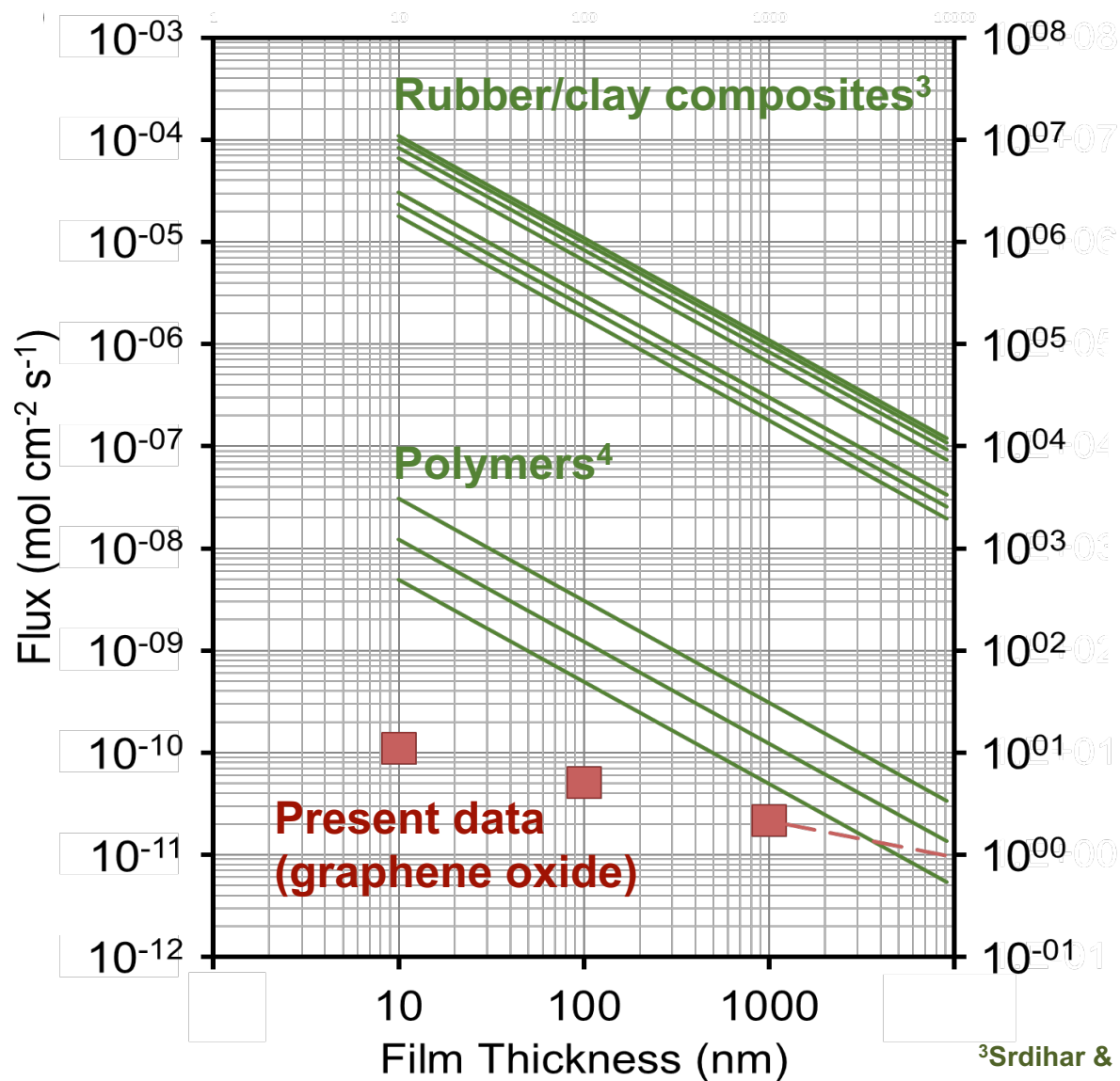
Results: Breathability and Toxicant Permeation



¹Bui et al, Adv Mater, 2016

² Wartell et al, 1999

Results: TCE permeation performance relative to other materials



Graphene oxide films are promising barriers (for TCE), especially in ultrathin/light applications

³Srdihar & Tripathy, J Appl Polym Sci, 2006

⁴McWatters & Rowe, J Geotech Geoenviron Eng, 2010

Modelling: What toxicant and film properties govern permeation?

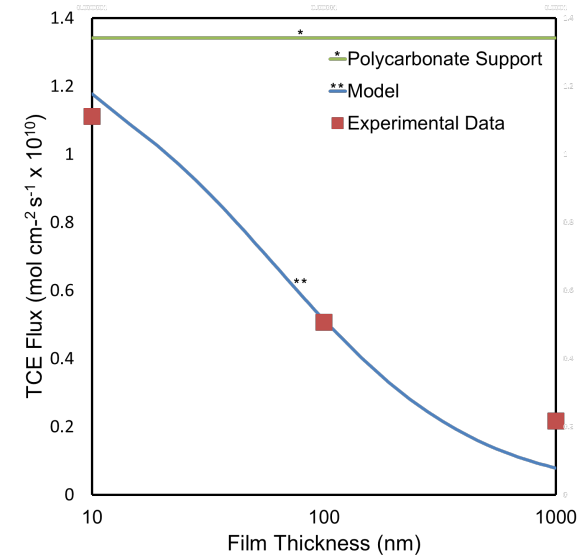
Generation 1 model

$$(VC_A)_x + \left(-D \frac{dC_A}{dx}\right)_{x+\Delta x} = (VC_A)_{x+\Delta x} + \left(-D \frac{dC_A}{dx}\right)_x$$

$$\dot{N}_A = K_{total} \Delta C_A$$

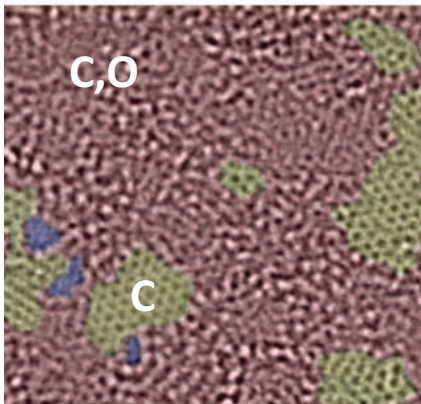
$$\text{where: } \frac{1}{K_{total}} = \frac{1}{K_{baseline}} + \frac{1}{K_{gallery} + K_{pore}}$$

Predicts no back-diffusion
of TCE against water flux (??)

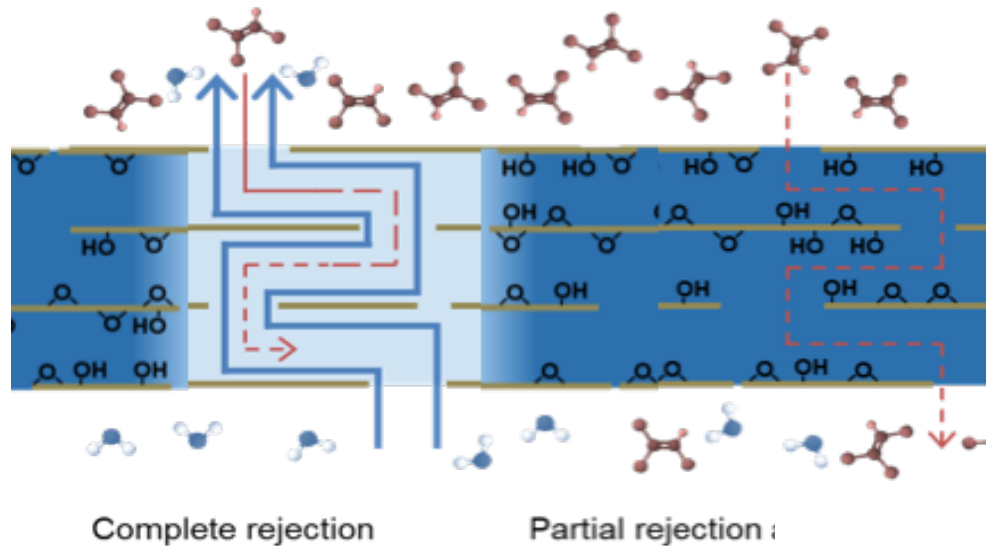


Generation 2 model

GO: oxidized and pristine domains



Erickson
et al.,
Adv Mat



Graphene Environmental Barriers: Summary

- > The ideal graphene sheet is a perfect molecular barrier
- > Commodity graphene nanosheets can be practical barriers as multilayers (> 10).
Most attractive for ultrathin/light applications
- > Graphene oxide films have enlarged intersheet “gallery” spaces and show complex behaviors in wet conditions
- > Graphene oxide films show ultra-high “breathability” (water permeation), and exclude agents larger than 0.9 nm (bacteria, viruses, particles, most molecules)
- > Barrier performance against small molecule toxicants depends on water solubility (effective for TCE, less effective for EtOH)
- > Graphene oxide offers promise as an active layer in breathable protective technologies, but more work is needed

